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# Economic Geology

and the

## Bulletin of the Society of Economic Geologists

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# Economic Geology

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# ECONOMIC GEOLOGY

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## GEOLOGY OF THE BRADEN OREBODY, CHILE, SOUTH AMERICA


FRED H. HOWELL AND JOHN S. MOLLOY


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ABSTRACT

The El Teniente Mine of the Braden Copper Company, 45 miles southeast of Santiago in central Chile, is the largest underground copper mine in the world. Although the immense Braden orebody has been exploited on a large scale since about 1908, the only published description of the deposit stems from a brief examination by Lindgren and Bastin in 1917. Since that time, extensive exploratory and development work have provided a wealth of new evidence. This paper presents a description of the deposit and conclusions regarding its origin based upon a recent three-year study of the orebody and its environs.

Bedrock near the mine consists mostly of extensive volcanic flows and intercalated terrestrial sediments containing numerous unconformities and disconformities. These rocks are correlated with the Tertiary (?) Farellones formation, a recently-established stratigraphic unit that includes the uppermost portion of an extremely thick (50,000+ feet) series of rocks deposited in the Andean Geosyncline during Mesozoic and early Tertiary time. These rocks, predominantly andesites, have been broken by strong northeast-striking faults and intruded by quartz diorite, dacite porphyry, and hornblende lamprophyre.

The most prominent structural feature in the mine area is the Braden Pipe—a circular, downward-tapering hole in the volcanics, filled with a breccia, and surrounded by the orebody. It is believed that the Braden Pipe developed after ore deposition and upon the site of an older stock of dacite porphyry. There seems to have been intermittent vertical displacement of the fragmental pipe-filling material, herein termed Braden formation, relative to the surrounding rocks. This displacement was probably both upward and downward, but the final movement was a substantial subsidence of material within the pipe.

Hydrothermal rock alteration appears to be comparatively mild, but indirect evidence suggests that the most intensely altered rocks may have been destroyed in the evolution of the Braden Pipe. The most obvious remaining alteration is the development of plentiful fine-grained secondary biotite throughout the andesite within the orebody.

Metallization was probably more or less continuous, but at least five distinct stages can be recognized. The first was a relatively unimportant deposition of quartz and a little pyrite in the northeast-striking faults. The second stage includes the main deposition of chalcopyrite and bornite with a quartz-anhydrite gangue. The third and fourth stages are characterized by abundant tourmaline with minor sulfides. The fifth and final stage deposited relatively unimportant amounts of tennantite, galena, and sphalerite in a quartz-carbonate gangue. Subsequent supergene enrichment has increased the original grade of primary ore almost twofold.

In comparing Braden with other mining districts, the Braden orebody, in spite of some apparent anomalies and structural peculiarities, seems to be almost a model porphyry-type deposit. The interrelationships of intrusive activity, breccia pipe formation, hydrothermal rock alteration, stockwork fracturing, and metallization are especially well illustrated and suggest certain generalities that might be applicable to all porphyry-type deposits.

## INTRODUCTION

THE El Teniente Mine of the Braden Copper Company is on the western flank of the Andean Cordillera in central Chile. It is the southernmost of the big South American porphyry copper mines, and in daily production, it is the largest underground copper mine in the world. Between 1906 and 1959 the immense orebody has yielded almost 300 million tons of ore averaging approximately two percent of copper.

To the economic geologist, the Braden orebody presents a rare opportunity to observe, and a challenge to decipher, many details of ore deposition. This paper presents a description of the orebody and conclusions regarding its origin based upon a three-year geologic research project initiated in July, 1956 by the Operating Properties Division of the Kennecott Exploration Department.

*Previous Work.*—Considering its size and economic importance, published information on the Braden orebody is relatively meager. The earliest description of the deposit is a paper by Lindgren and Bastin (1) based upon a short examination in 1917. They concluded that the salient event in the orebody's history was a violent explosion that produced a deep volcanic crater and shattered the surrounding andesite, thereby providing ample open spaces for subsequent deposition of ore minerals. They also visualized a rather complex sequence of metallization with an intervening intrusion of alkali porphyry breccia.

Brüggen visited Sewell briefly in 1932, and without collecting any significant new evidence, he interpreted the data of Lindgren and Bastin quite differently (2). He questioned the volcanic explosion origin of the "crater" and proposed a more plausible sequence of mineral deposition.

*Field Work and Scope of Paper.*—During the three-year period, surface geology in the vicinity of the mine was mapped on a scale of 1:2,500, accessible underground workings were mapped on 1:1,500-scale, and all available diamond drill core was logged. Reconnaissance traverses and aerial flights over the mine area helped to establish the regional setting. Topographic maps for the field work were prepared photogrammetrically from aerial photographs of the region. Petrologic classifications and paragenetic relationships were determined from the examination of more than 400 thin and polished sections, and from chemical analyses of selected rock and mineral specimens.

Colored ore zone overlays on acetate tracing film were compiled from channel samples and diamond drill hole samples and accompany each geologic plan and section map.

Data accumulated from these and other sources have led to conclusions

that differ importantly from those reached by Lindgren and Bastin. The work has also yielded prompt and substantial economic returns.

In a sense, this paper should probably be regarded as a preliminary report. With an orebody as large and complex as the Braden deposit, two geologists within a three-year period could, in effect, do little more than work out the geologic essentials and lay a foundation upon which detailed studies might follow. A resident geology department has now been made an integral part of the Braden operation, and thus the conclusions presented in this paper will be subject to subsequent modification or substantiation by continuing geological studies.

FIG. 1. Index map showing mine and installations of the Braden Copper Company.

Because this paper was prepared in Chile and without access to a geological library, the literature could not be reviewed as would have been desirable, hence relatively few references are given.

## LOCATION AND GENERAL SETTING

The Braden Mine is at Sewell on the western slope of the Andes Mountains, 45 miles southeast of Santiago, the capital of Chile (Fig. 1). Operations of the Braden Copper Company are dispersed throughout much of the Rio Cachapoal watershed. The various camps are connected by a narrow-gauge, company-owned railroad that terminates at Rancagua, a town of 50,000 inhabitants in the heart of Chile's fertile Central Valley, about 50 miles south of Santiago.

From Rancagua, the railroad runs eastward up the Cachapoal Valley for 18.8 miles to Coya, near where are located the two hydroelectric plants that supply power for all of the company's operations. At Coya the railroad leaves the Cachapoal Valley and follows a tributary, the Rio Coya, northward for 16.3 miles to Caletones, the smelter camp, at an altitude of 5,100 feet. From Caletones, the railroad continues up the narrow precipitous gorge of the Rio Coya to Sewell at an altitude of 7,000 feet, 43 miles from Rancagua. Sewell has about 11,000 inhabitants and is the main camp for the mine and mill (Fig. 2).

FIG. 2. Photograph of Sewell with Braden Pipe and Mine area in upper right.

The orebody crops out on the steep slope southeast of the Rio Teniente, about 1½ miles east of Sewell.

The highest peaks in the Sewell area are near 12,400 feet in altitude and are remnants of an old westward-sloping volcanic plain. All drainage is generally to the west. The many streams and rivers, fed by heavy winter snowfall, originate from glacial lakes and perennial snowbanks in cirque basins, and follow U-shaped valleys along their upper portions. At lower altitudes the watercourses have cut deep V-shaped valleys, reflecting strong recent uplift.

Average annual precipitation at Sewell is about 42 inches, most of which falls as snow between May and September. Annual snowfall averages about 21 feet, but the relative humidity is very low throughout the year. Due

to the scarcity of rain and the steepness of the terrain, there is almost no vegetation above 6,000 feet of altitude.

## HISTORY AND DEVELOPMENT

In Chile, the Braden Mine is called the El Teniente Mine, the name originating from its legendary discovery in 1706 by a fugitive Spanish army lieutenant (*el teniente* in Spanish). The first official records of ownership and production are for the year 1819. From the time of its discovery until 1903, small amounts of high-grade ore were mined intermittently from shallow workings by primitive methods, the ore being hand-sorted and transported by mule to the coast. As very little ore contained more than 4 percent of copper, it soon became apparent that successful exploitation of the deposit would require facilities for concentrating the ore. In 1903 William Braden and E. W. Nash, then president of the American Smelting and Refining Company, acquired interests in the property, and in 1904 they formed the Braden Copper Company. A 35-mile wagon road was built to the mine from Graneros in the Central Valley, and in 1906 construction of a 250-ton per day concentrator was completed. The railroad from Rancagua was started in 1906 and finished in 1911. The property was taken over by the Guggenheim interests in 1908 and the whole plant capacity raised to 5,000 tons per day. In 1915 the Kennecott Copper Corporation acquired a controlling interest, and since then, plant capacity has gradually been increased to about 34,000 tons per day.

Ore is mined by block caving and transferred by gravity through an extensive ore-pass system downward to No. 5 level, the lowest and main haulage level. Production rate is governed by the availability of water, both for the mill and for the generation of electric power. During the coldest part of the winter when run-off is very low, production is restricted, the lowest rate being about 22,000 tons per day. Recent annual mine production is about 11 million tons of ore. The ore possesses ideal characteristics of caving well when undercut, and yet the rock stands satisfactorily in underground workings. The mine has been explored and developed by more than 500 miles of recorded horizontal and vertical workings and by considerable diamond drilling, covering an area more than a mile in diameter and extending to a depth of 5,000 feet below the outcrop.

## REGIONAL GEOLOGY

The geologic history of the Andean Cordillera in central Chile begins in the Jurassic Period and is a story of rapid and prolonged geosynclinal deposition, punctuated by marine transgressions, orogenic disturbances, and periods of intense volcanic activity. Early in the Mesozoic Era a long narrow trough of intermittent subsidence—the Andean Geosyncline—developed along the western margin of the Brazilian Shield, approximately in the same place now occupied by the Andes. During the Mesozoic and early Tertiary, a tremendous thickness—at least 50,000 feet—of volcanic extrusive rocks with intercalated terrestrial and marine sediments accumulated in this geosyncline.

Subsequent strong uplift, associated with the intrusion of the Andean Batholith, elevated this synclinal filling to form the Andean Cordillera. Charles Darwin (3), in 1837, named this thick column of heterogeneous rocks the "Porfiritica Formation," and until recently, no attempt has been made to subdivide it into lithologic units. The term has served as a convenient "catchall" in the Chilean geologic literature.

In 1953 Klohn (4) initiated studies to divide the Porfiritica Formation in the central Cordillera into mappable units. He has established a tentative subdivision comprising six formations, with fourteen stratigraphic members (Fig. 3). Interformational boundaries are fixed by the upper and lower

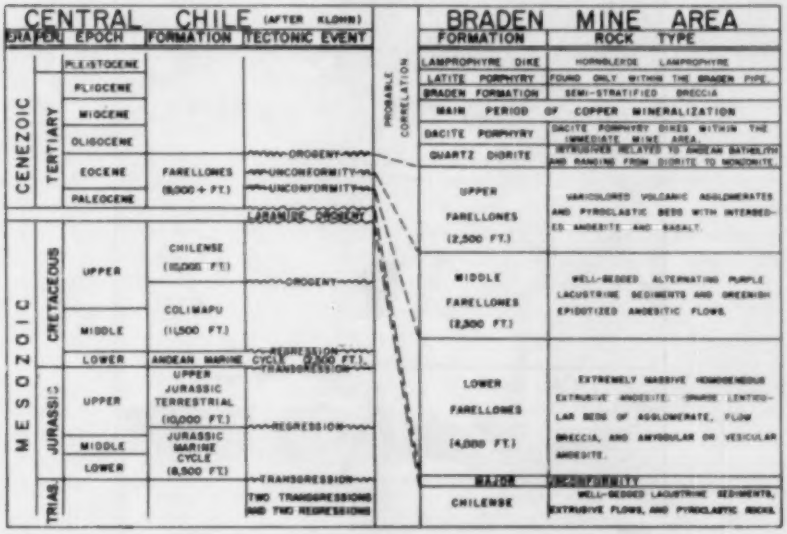


FIG. 3. Correlation of stratigraphic units in the Braden Mine area.

limits of marine sedimentation, by angular unconformities, or by erosional disconformities. Klohn lists four marine transgressions and regressions during the Mesozoic, with the final regression at the close of the Lower Cretaceous, followed by three major orogenies. He correlates the middle orogeny at the close of the Mesozoic with the Laramide Orogeny in North America.

Except for intrusive rocks, all bedrock in the Sewell-Coya region belongs to the Chilense and Farellones formations (Fig. 4).

The Upper Cretaceous Chilense formation occurs in two north-trending belts, each from 5 to 8 miles wide, and separated by about 18 miles of overlying Farellones formation. The Chilense consists of extrusive flows, porphyritic pyroclastic rocks, and well-bedded lacustrine sediments. The beds are folded, and steep, locally-divergent dips are common.

The top of the Chilense is marked by a conspicuous angular unconformity, above which lie tilted and gently folded strata of the Farellones formation. In the Sewell area the Farellones is the predominant formation and contains at least six angular unconformities. The two with the largest discordance have been used to divide the formation into three members. The lowest

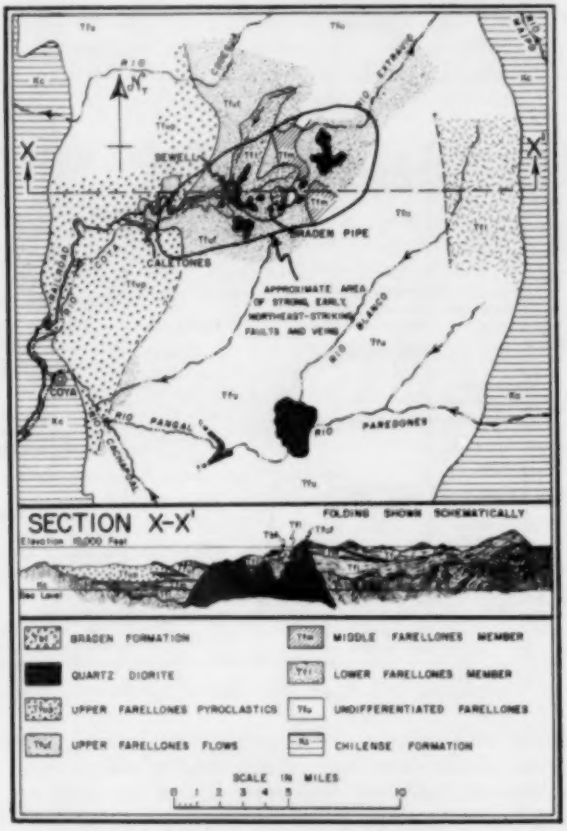


FIG. 4. Regional geology surrounding the Braden Mine.

member is the host rock for most of the orebody and consists of massive andesite containing lenses of flow breccia and other sparse evidence of its extrusive origin. The middle member comprises well-bedded epidotized andesitic flows and purple lacustrine sediments. The top member contains abundant agglomerates and pyroclastic beds, with intervening flows of andesite and basalt.

The Braden orebody lies near the center of the Andean Geosyncline in

a well-defined belt of intrusive stocks, dikes, and sills about 12 miles wide. Volcanic beds within this belt are conspicuously disrupted and distorted. Although individual intrusive masses differ somewhat in composition and texture, the predominant rock type is quartz diorite, suggesting a common genetic relationship to the underlying Andean Batholith. The center-line of the belt lies about 28 miles west of the continental divide. To the east of the belt, gently-dipping volcanics predominate, pierced at intervals by volcanic cones along the crest of the Andes.

## ROCK TYPES AND PETROGRAPHY

When surface geologic mapping was started during the 1956–1957 field season, virtually no geologic maps of the central Chilean Andes were available. In the region surrounding the Braden Mine we found a thick series of volcanic extrusive rocks and terrestrial sediments, invaded by various intrusive rocks. Chilean geologists considered this section, which exceeds 20,000 feet in thickness, to be a part of the ill-defined Porfiritica Formation. This classification in itself was hardly suitable, for in order to work out the structural setting of the orebody, smaller, more precise, mappable rock units were needed. Based upon lithology, structural traits, conditions of sedimentation, and orogenic discordances, four major subdivisions were recognized. However, as none of these rocks contains diagnostic fossils, the resultant scheme could not be correlated with the geologic time scale.

With the publication of Klohn's preliminary report (4) in 1957, there existed a more comprehensive framework with which our local map units could be correlated (Fig. 3). However, due to the size and ruggedness of the area, the rapid lateral lithologic changes within individual beds, the occasional absence of certain units, and in some places the scarcity of good exposures, it was usually impossible to make direct visual correlations. The relationship shown in Figure 3 is based largely upon a matching of similar sequences of analogous rock types and upon the tracing of unconformities of differing discordance. With only such indirect evidence, and lacking any ready means of determining absolute age, the chronology of the stratigraphic units in the Braden Mine area should probably be regarded as somewhat provisional. Subsequent more extensive field work will undoubtedly provide a more precise definition.

### *Volcanic and Sedimentary Rocks*

*Chilense Formation.*—The oldest of the four stratigraphic units in the Braden area corresponds to Klohn's Upper Cretaceous Chilense formation. Its limits are unknown, but probably the Chilense occurs in much of the area formerly occupied by the Andean Geosyncline. In the drainage basins of the Rio Cachapoal and Rio Maipo, strata of the Chilense formation occur in two north-trending belts, each from 5 to 8 miles wide (Fig. 4). The Chilense does not occur within 10 miles of the Braden Mine, but it probably underlies the orebody at moderate depth. Good exposures of well-bedded Chilense can be seen along the Braden railroad both to the north and to the south of Coya.

As the Chilense formation is only remotely related to the Braden orebody, it was not mapped nor studied in much detail. In the exposures near Coya, alternating beds of lacustrine sediments and volcanic extrusive rocks range in thickness from a few inches to several feet and show prevailing gray, purple, and brown colors. The beds are commonly rather tightly folded so that dips are local and generally steep. Sedimentary beds range from siltstones to conglomerates and lack lateral continuity. The volcanic beds are usually thicker and of variable composition, including andesite, basalt, agglomerate, and pyroclastic beds.

The top of the Chilense formation is marked by a prominent angular unconformity, and Klohn (4) reports that the bottom of the formation is similarly represented. Although no fossils have been found in the Chilense, Klohn's assignment of it to the upper Cretaceous is based upon indirect, but good, evidence. Total thickness is approximately 10,000 feet. Apparently the upper Cretaceous in central Chile was a time of crustal unstability and intermittent volcanic activity.

*Farellones Formation.*—The uppermost part of the old Porfiritica Formation conspicuously covers a large area of central Chile and corresponds to Klohn's Farellones formation. Except for later intrusive rocks, bedrock within several miles of the Braden Mine comprises more than 9,000 feet of heterogeneous volcanic rocks that are tentatively correlated with the early Tertiary (?) Farellones formation. We have subdivided this thick column of rock into three distinctive lithologic members, separated by angular unconformities. Each member also contains one or more additional unconformity of lesser discordance. As this subdivision has not been used before, the relative distribution and thickness of the three members of the Farellones are unknown outside of the Braden Mine area. The early Tertiary in central Chile followed the prominent hiatus corresponding to the Laramide Orogeny and must have been a time of strong tectonic disturbance accompanied by intense volcanic activity and periods of rapid erosion.

Outcrops of the *lower Farellones* member of the Farellones formation, exposed through a window in the younger rocks, are confined to within a few miles of the mine, where they have been mapped and studied in considerable detail. The lower Farellones seems to be missing above the belt of Chilense west of Sewell, but to the east, the massive cliffs along the upper tributaries of the Rio Cachapoal probably belong to the lower Farellones. The following description is confined to the lower Farellones exposed near the mine.

The lower member of the Farellones formation is the principal host rock of the orebody and consists almost entirely of massive extrusive andesite. Being the oldest stratigraphic unit in the mine area, it is found in topographic lows where it crops out along the lower slopes of both the Coya and Teniente Canyons for several miles above and below Sewell. The bottom is nowhere exposed, even in the deepest drill holes and workings in the mine. The top is marked by a prominent angular unconformity that undulates gently and dips flatly to the southwest. Maximum exposed vertical thickness is about 4,000 feet, but its true thickness, measured normal to the beds, is probably less.

The andesite is homogeneous and extremely massive so that evidence of its extrusive origin is usually difficult to find. This is probably why Lindgren and Bastin considered the andesite to be an intrusive rock. Detailed mapping has shown, however, that it contains agglomeritic flows, lenticular beds of flow breccia, and sparse amygdaloidal and vesicular layers. Most of these features are very effectively masked in the immediate mine area by abundant secondary biotite. Outcrops are iron-stained and appear to be very massive, but generally the rock is well broken by jointing, minute fractures, and closely-spaced sheeting. Without the sparse extrusive features, it is almost impossible to detect the bedding. However, enough bedding has been recognized and mapped to show that the lower Farellones in the Sewell area has been rather broadly folded, with dips ranging up to 60 or 70 degrees. These flexures have north-trending axes that parallel the regional structure.

Except for its extreme thickness, the lower Farellones andesite is almost identical with other extrusive andesites, both older and younger, throughout the Cordillera. Where fresh, it is dark gray and ranges in texture from an aphanite to a fine-grained porphyry with phenocrysts up to 3 mm long. Flow structure is quite common. The feldspar of both groundmass and phenocrysts is andesine or labradorite. Ferromagnesian minerals are hornblende and less abundant augite, both generally strongly altered to chlorite and epidote. Magnetite, probably titaniferous and commonly altered to leucoxene, is the predominant accessory mineral, and apatite is locally abundant. Quartz and potash feldspar are almost completely absent.

In the peripheral area surrounding the orebody the andesite may show a moderate propylitic alteration with abundant calcite, epidote, and chlorite, giving the rock a light-green color. Throughout the orebody, and for some distance beyond its boundaries, the andesite is flooded with a fine-grained secondary biotite that can be recognized megascopically by a characteristic silky sheen on freshly fractured surfaces. Within the orebody, the andesite in places is strongly silicified for several feet from contacts with the intrusive quartz diorite. On the upper levels the andesite may be strongly argillized and/or sericitized, probably by surficial alteration, to a white or light-gray punky material.

The *middle Farellones* member occurs in a single northwest-trending belt about one-half mile wide just north of the mine. Elsewhere in the area, it is missing between the upper and lower members. As the middle Farellones has no important bearing upon the orebody, its description will be brief.

Above the prominent unconformity on top of the folded lower Farellones lie about 2,500 feet of gently tilted strata of the middle Farellones. This member consists of alternating beds of greenish epidotized andesitic volcanics and brownish-purple lacustrine sediments. Average thickness of individual beds is about 5 feet. As the member contains numerous angular unconformities of slight discordance, the strike of the beds is variable, but the dip seldom exceeds 30 degrees. The top of the middle member is marked by another angular unconformity that is also an erosion surface of considerable relief.

Flat-lying fresh volcanic beds of great variety form most of the ridge tops in the Sewell area and belong to the *upper member* of the Farellones forma-

tion. It is the predominant rock type throughout most of the Rio Cachapoal and Rio Maipo drainage basins and comprises a section at least 2,500 feet thick. It rests unconformably on both the middle and lower members; the top has not been found in the Sewell area. None of the orebody occurs in the upper Farellones, but at one time, before erosion had removed the upper part of the orebody, the upper Farellones member was probably an important host rock. It is characterized by multicolored flows of andesite and basalt intercalated with agglomerates and pyroclastic beds, all dipping rather uniformly from 8 to 12 degrees to the south. To the west, along a north-trending line through Caletones, these prominent beds give way abruptly to an undetermined thickness of pyroclastic material that lacks sorting and is only slightly consolidated. This fragmental rock seems to be a lateral facies change of the upper Farellones, but it may also be partly younger.

*Braden Formation.*—The Braden formation includes all of the detrital material that fills the Braden Pipe—the most prominent structural feature associated with the orebody. The Braden Pipe is described in detail below under *Structure*. It will suffice to say here that the Braden Pipe is a circular, downward-tapering hole in the volcanic rocks about 4,000 feet in diameter at the surface, which has been filled with a variety of rock debris and is surrounded on all sides by the Braden orebody.

This pipe-filling material, which Lindgren and Bastin called the Braden Tuff, is fragmental, fairly well-consolidated, and although the larger fragments are all rounded, it is in truth a breccia. The fresh material is light gray and resembles broken concrete. On the surface, iron oxides color it rusty brown. The difference in particle size is extreme, ranging from sub-microscopic rock and mineral particles to rounded boulders several feet in diameter. Most of it is completely unsorted, but in some places, particularly on the surface, a crude bedding can be seen. Even where the rock is well-bedded, however, thin-sections show no conclusive evidence of sedimentation, for all of the smallest particles are markedly angular, and sorting has been very imperfect. Yet, in an area on the surface in the western portion of the pipe, this bedding is well-developed and so extensive and so consistent in attitude that the operation of some sedimentary sizing action can hardly be denied. It might be inferred that while the Braden formation was being deposited, a shallow lake existed intermittently within the Braden Pipe. The bedding must have been horizontal at one time, but it now dips everywhere toward the center of the pipe, being steepest near the edges and flattest in the middle.

The fragments consist largely of the same rock types that occur around the margins of the pipe, but some, including a few chert fragments, are clearly extraneous. A significant feature is the abundance of ore fragments throughout the Braden formation. Around the margins of the pipe they are plentiful enough to make mineable ore, and throughout the remainder of the pipe the average copper content is between 0.2 and 0.3 percent, with a decided increase in depth. The ore fragments range in size from the smallest particles to the largest boulders, and invariably the ore minerals are fresh primary sulfides. Another important feature of the Braden formation is the gradual downward

increase in the number of fragments of quartz diorite and dacite. Some of these fragments are fresh; others are strongly altered and contain abundant fresh chalcopyrite. The Braden formation also contains sparse tiny veinlets carrying gypsum and late-stage sulfide mineralization.

### *Intrusive Rocks*

*Andesite.*—The only known intrusive andesite found in the whole Sewell area is confined to a few small dikes in the middle and upper Farellones about a mile northwest of the mine. Petrographically, it is a fine-grained porphyry identical to most of the extrusive andesite. In outcrops, however, the intrusive andesite is less fractured and sheeted, and it weathers to a distinctive white, pock-marked surface. Original composition, now somewhat changed by moderate propylitic alteration, was about 65 percent labradorite-andesine, 27 percent hornblende, and 8 percent magnetite. In age, it is younger than the lower part of the upper Farellones; lacking any other age relationships, it cannot be dated more closely. It is probably related, maybe as feeder dikes, to some of the later andesitic flows.

*Quartz Diorite.*—Stocks, dikes, and irregular masses ranging from diorite to monzonite are scattered throughout the intrusive belt described above under *Regional Geology*. The largest mass is an elliptically-shaped stock about 8 miles long on the Rio Maipo, 20 miles north of Sewell.

Outcrops are massive, light-gray to white, and generally smoother and more rounded than those of the volcanic rocks. The nature of the contacts varies with the size of the intrusion. Dikes and small masses generally have sharp boundaries; the larger intrusions have gradational contacts several feet wide. The quartz diorite apparently invaded the volcanic rocks in a passive manner, for there is no evidence of it having folded or otherwise disrupted the extrusive beds.

Fresh quartz diorite from outside the mine area generally has a medium to fine-grained hypidiomorphic texture, but some is porphyritic with up to 40 percent of groundmass. Plagioclase, biotite, hornblende, and quartz can be recognized in hand specimens. Some varieties contain large scattered pink orthoclase crystals up to 1 cm in length. The plagioclase is mostly andesine, averaging about 2 to 3 mm in grain size; ferromagnesian minerals are predominantly hornblende and biotite, with minor augite. Orthoclase and quartz each make up about 15 percent of the fresh rock, and apatite, magnetite, zircon, and sphene are the common accessory minerals. All thin sections show slight to moderate alteration to chlorite, epidote, calcite, and magnetite, with minor sericite.

Near the orebody, the texture is generally more porphyritic with an average of about 20 percent groundmass. The plagioclase is commonly albite, and orthoclase is very scarce. Biotite and hornblende are strongly altered to chlorite and are much less conspicuous than in the fresh rock. Argillation and sericitization are locally very strong, and due to the attendant release of free silica, quartz makes up much of the groundmass. Chemical analyses

of the altered quartz diorite from within the orebody show 63 percent silica, indicating a mineralogical rearrangement, but no substantial increase in silica over the comparable fresh rock. Alumina remains about the same, but all of the bases have been noticeably extracted by alteration.

The quartz diorite can be assigned an age relative to other rocks in the area, for it intrudes the upper Farellones member, and in turn, is cut by dikes of dacite porphyry.

*Dacite Porphyry.*—Dacite porphyry occurs in relatively small amounts and is restricted to within a mile of the mine. It is important genetically for it seems to be very closely associated in age with the main period of copper mineralization.

The largest mass of dacite porphyry is a dike about 400 feet wide extending almost due north from the Braden Pipe for about a mile. Another much smaller dike is found about a mile southwest of the mine, and other small discontinuous dike segments exhibit a tendency to encircle the Braden Pipe. In the latter case, the dikes resemble cone sheets, for they nearly always dip inward toward a common center.

The dacite porphyry is a fairly massive, almost white rock characterized by prominent black biotite books, rounded glassy quartz eyes, and cream-colored altered feldspars in a white aphanitic matrix. The feldspar phenocrysts are albite-oligoclase, and a little orthoclase is in the groundmass. Normally the groundmass constitutes from 30 to 60 percent of the rock. Apatite, zircon, magnetite, and sphene are common accessory minerals. In narrow dikes and along margins of the wider dikes the dacite porphyry is commonly finer-grained, darker, and more basic than usual. Here, biotite is more abundant, a little hornblende appears, the plagioclase grades into andesine, quartz content decreases, and the proportion of groundmass increases. Most of the dacite porphyry, especially in the wider dikes, has been strongly silicified, accompanied by moderate to strong chloritic alteration of the biotite and sericitization of the feldspars and groundmass.

Absolute age of the dacite porphyry is unknown, but we can bracket its relative age, for it cuts the quartz diorite, and is, in turn, cut off by the Braden Pipe. In some occurrences the dacite porphyry closely resembles the more porphyritic facies of quartz diorite. There might be a close genetic relationship between the two, with dacite porphyry representing a later, more acid fractionation of the quartz diorite magma.

*Latite Porphyry.*—Latite porphyry is restricted to the Braden Pipe where it occurs as irregular autobrecciated masses that are both concordant and discordant in relation to bedding in the Braden formation. The latite is somewhat enigmatic, and its precise mode of origin is still uncertain. Lindgren and Bastin attached great importance to the latite and considered it to be an intrusive breccia that had been forced upward around the margins of the pipe. Mine workings and diamond drill holes now show that the latite is most abundant on the surface and that at depth it is restricted to one or more relatively small intrusive passageways.

Where bedding in the Braden formation is well-developed, latite porphyry occurs as tabular conformable masses that could be either intrusive sills or

extrusive flows. Existing evidence is inconclusive. Other occurrences of latite porphyry have steeply-dipping contacts and seem to be irregular pipe-like intrusions.

All of the latite porphyry, except for a small portion in the interior of the largest masses, is typically autobrecciated. Rounded to sub-rounded fragments up to several feet in diameter characteristically occur in a matrix of the same rock. Nearly all contacts between latite porphyry and Braden formation are ill-defined and gradational. The Braden formation contains an increasingly greater proportion of latite fragments of larger size as latite masses are approached.

The rock is variable in appearance, ranging in color from dark green to light green or white. It is characterized by a medium to coarse-grained porphyritic texture, with phenocrysts of andesine-labradorite, orthoclase, hornblende, and sparse biotite and quartz in an aphanitic groundmass that makes up about 60 percent of the rock. Most of the latite porphyry is unmineralized, but in places it does carry pyrite and sparse veinlets of late-stage enargite-chalcopyrite mineralization. Emplacement of some of the larger masses was accompanied by strong tourmalinization. Near contacts between latite porphyry and the Braden formation, tourmaline has replaced the matrix of both rock types in varying degrees.

Generally the latite porphyry is so strongly altered to sericite, chlorite, and calcite that precise petrographic classification is impossible. However, it is clear that there are several varieties, and that its emplacement took place intermittently over a considerable period of time. Well-rounded fragments of latite scattered abundantly throughout the Braden formation represent a rock that must be appreciably older than the latite masses described above.

*Lamprophyre.*—A single narrow hornblende lamprophyre dike is the youngest intrusive rock. Although it averages only 6 feet in width, it is very persistent and cuts across the southeastern part of the orebody on every level in the mine. It generally occurs in detached segments arranged *en echelon*. Near Sewell, it is restricted to the immediate mine area, but it reappears again near Caletones.

Underground exposures are blocky and strongly iron-stained and show prominent flow structure parallel to the dike margins. The rock is a fine-grained, dense, gray-black porphyry with hornblende needles about 1 mm long the only megascopically visible constituent. About 85 percent of the rock is microcrystalline groundmass with the remaining 15 percent consisting of hornblende needles and tiny sparse phenocrysts of augite and labradorite. A little olivine, partly altered to iddingsite, is present. Alteration products are mainly chlorite and calcite. Augite is altered to hornblende and chlorite; the hornblende is partly bleached, but otherwise fresh. The lamprophyre also contains a little pyrite and copper. Both cuprite and native copper are found as sparse cavity fillings and are undoubtedly of secon lary origin.

The lamprophyre is clearly post-ore and also later than the Braden formation, which it cuts. There is no apparent means of determining how young it might be.

## STRUCTURE

### *Folding and Early Faulting*

Folding in relation to the Braden orebody is not significant, but it serves as a helpful guide in recognizing and correlating the various rock units. The Chilense formation is locally tightly folded, whereas the overlying lower Farellones member shows only broad flexures. Younger beds are commonly tilted, but exhibit folding only as local drag folds near faults. Most of the fold axes strike northward, parallel to the regional structural trend.

The existence of an early crustal weakness in the Sewell area is shown by a prominent northeast-striking set of strong faults and veins. Original movement on them dates back at least to early Farellones time, and they clearly show that displacement has been intermittent and recurrent. The average strike is about N 55° E, so that they intersect the regional tectonic alignment at an angle of about 50 degrees. These faults and veins are more or less centered upon the Braden Pipe. They occur prominently for about 2 or 3 miles to the northwest and southeast on either side of the pipe and continue to the northeast and southwest along strike for 6 or 7 miles, gradually dying out or disappearing beneath younger rocks. The faults generally dip away from the Braden Pipe, and where offsets can be recognized, the displacement is mostly rather small and in a normal direction. The cumulative effect has been an upthrusting near the center of the faulted area, which has left the northwest side relatively lower than the southeast side.

The veins contain quartz, hematite, and barite, with sparse sulfides—generally pyrite. Near the Braden orebody, they have no commercial value, but in outlying areas, more than a mile from the mine, galena and sphalerite with minor chalcopyrite and pyrite may occur in mineable amounts.

These veins show a marked difference in apparent strength in each of the three members of the Farellones formation. In the lower Farellones, the veins are strong and prominent. They make conspicuous outcrops of iron-stained quartz up to 30 feet wide that stand above the surrounding rocks. Generally the quartz is shattered or brecciated, and its texture resembles that of granulated sugar. As these veins pass upward across the unconformity into the middle Farellones, there is an abrupt diminution in width and brecciation. In most places the middle Farellones is missing, and the change in veins passing from the lower to the upper member of the Farellones formation is even more striking. As an example, a vein in the lower Farellones containing 20 feet of iron-stained granulated quartz might appear in the middle Farellones as a vein with 4 feet of vuggy quartz. In the upper Farellones member, this same vein would appear as a weak fault with not more than 2 or 3 feet of bleaching and iron-staining. We can conclude from this evidence that there were at least three periods of movement on these faults, one following deposition of each of the three Farellones members.

### *The Braden Pipe*

The most spectacular structural feature of the ore deposit is the Braden Pipe. Essentially, it is an inverted cone of Braden formation in the lower

Farellones member, surrounded by the orebody. Figures 5, 6, 7, and 8 illustrate its size and shape and its relation to other rock types.

Although its exact mode of origin is still uncertain, there is no direct evidence that the Braden Pipe ever served as a conduit for the ejection of any appreciable volcanic material. Not even its association with volcanism can be proved. For this reason, the term "pipe" seems more appropriate than Lindgren and Bastin's "crater." Even "pipe" admittedly leaves something to be desired, but no better terminology seems to exist. For like reasons, Lindgren and Bastin's "Braden Tuff" has been replaced by "Braden formation."

The Braden Pipe is almost circular in plan and has a diameter at the surface of about 4,000 feet. The east side is almost vertical; the other sides all dip inward, the west side being the flattest with a dip of about 60 degrees. The pipe thus resembles an inverted, tilted cone with a vertex angle of about 30 degrees. Its known vertical extent from the highest surface outcrop to the lowest exposure in a diamond drill hole is more than 5,200 feet.

Around the margins of the pipe are found two distinctive breccias of different ages. The earlier one, herein called pre-pipe breccia, occurs as a nearly continuous belt in the various rocks adjacent to, but outside of, the actual pipe. The width of the breccia is variable, but it averages between 100 and 200 feet, being noticeably wider in the quartz diorite than in the andesite. Generally the outer limit of the breccia is surprisingly sharp. It is characterized by abundant fine-grained black tourmaline that has replaced the original matrix and which, in places, has also partly replaced the fragments. The tourmaline matrix in places contains a little chalcopyrite. Rounded pieces of this breccia are found throughout the Braden formation, and thus the breccia is earlier than the pipe. And, as the fragments are commonly silicified and contain abundant chalcopyrite, the breccia was formed after the main period of copper mineralization. This pre-pipe breccia seems to have resulted from the initial breaking-loose of the plug of rock that formerly occupied the Braden Pipe.

The later, or post-pipe, breccia reflects substantial displacement—mostly subsidence—of material within the Braden Pipe. It occurs within the Braden formation as a belt around the margin of the pipe, adjacent to, and just inside the ring of pre-pipe breccia described above. It is also found in irregular zones and stringers traversing the western third of the pipe. The contact between the brecciated and unbrecciated Braden formation is generally gradational and, in places, difficult to fix. This brecciated Braden formation typically contains bleached fragments, both rounded and angular, in a matrix that is slightly to completely replaced by fine-grained black tourmaline. The rock is commonly sandy or muddy in appearance and generally finer-grained than its unbrecciated counterpart. Apparently it has been subjected to additional comminution by the differential movement that took place along the margins of the pipe. A similar fine-grained facies can be found along faults within the Braden formation.

The actual boundary of the pipe thus corresponds to the contact between the pre-pipe and post-pipe breccias. The contact is obscure in many places,

but it can generally be established rather closely by noting the first appearance of fragments of more than one rock type in the breccia.

In addition to the breccias, several sets of joints and fractures that seem to be related to the Braden Pipe are found throughout the orebody. The most conspicuous ones have strikes tangent to the pipe and can be grouped roughly into four sets, depending upon the dip. One set dips outward away from the pipe at 41 degrees; the other three dip toward the pipe at 48, 65, and 84 degrees. These figures are averages of many individual observations. The sets that dip inward at 48 degrees and outward at 41 degrees include both joints and veinlets. The two steeper inward-dipping sets comprise joints, faults, and breccia zones. The eastern margin of the pipe apparently coincides with the set that dips 84 degrees, the western margin with the 65 degree-dipping set. Age relations suggest that the three inward-dipping sets developed during the initial upward push that served to localize the Braden Pipe. The outward-dipping set would have resulted from the subsequent relaxing of this force.

So far, no decisive evidence has been found to explain wholly the manner in which the Braden Pipe was formed. Several possible modes of origin can be postulated; the reader will have to choose one that is in keeping with his own experience and ideas. Lindgren and Bastin (1) described the Braden Pipe as a volcanic explosion crater which subsequently became a crater lake. Bruggen (2) attributed it to subsidence that dropped a plug of overlying volcanic agglomerate down into the older rocks. Neither interpretation is wholly in accord with the available evidence.

Any plausible mode of origin must take into account the following conditions:

(1) The pipe contracts with depth and is at least 5,200 feet deep. It may have been much deeper.

(2) The Braden formation, with which the pipe is filled, is actually a very homogeneous breccia.

(3) The Braden formation contains abundant fragments of ore and mineralized breccia. The pipe is therefore younger than the main period of copper mineralization.

(4) Except near the surface, sulfides in the ore fragments are exceedingly fresh.

(5) The pipe is surrounded by a pre-pipe and a post-pipe breccia.

(6) In some places the Braden formation shows an imperfect bedding that must be due to some sedimentary sizing action.

(7) Most fragments in the Braden formation seem to have come from the mineralized rock mass that formerly occupied the pipe. The rounding is well-developed in fragments exceeding 1 mm in diameter, but the matrix consists of tiny angular rock and mineral particles. The fragments must have been subjected to some abrasive process much more intense than merely rolling down a talus slope.

(8) The Braden formation was invaded by several stages of autobrecciated latite porphyry. Where bedding was well-developed, the latite porphyry

formed sills. Some of it may actually have been extruded as surface flows.

(9) Both the latite porphyry and the bedding in the Braden formation have been disrupted by later brecciation. The bedding consistently dips toward the center of the pipe.

It is clear that the site of the Braden Pipe was a center of strong mineralization and structural weakness before the pipe was formed in its present state. The early northeast-striking set of faults, the dacite dikes and cone sheet, and the orebody itself all pre-date the Braden Pipe. The structural evidence suggests that this center of crustal weakness was subjected to a strong upthrusting force which broke loose a conical plug of rock. The upward pressure might be attributed to some phase of the long orogenic history of the Andean Cordillera. Whether this force took the form of a violent explosion that completely removed the original rock plug, or whether the process was a more passive phenomenon, in which the plug was only loosened and perhaps brecciated, is not known. The latter alternative seems more likely, but the evidence is admittedly inconclusive.

The initial disruptive stage was followed perhaps by a period in which there may have been some pulsating movement within the pipe. There is no direct evidence for this other than the anomalous roundness of fragments within the Braden formation. The final stage is one in which the pipe-filling material subsided an undetermined, but substantial distance.

The most likely source of the inferred rising and falling prime force would seem to be the latite porphyry magma. The autobrecciated structure of the latite porphyry suggests a near-surface intrusion, and the time interval of latite porphyry intrusion is simultaneous with that period in which the pipe was formed. It might be postulated that the pipe connects at depth with a conduit which at one time contained an unstable column of latitic magma.

Several other much smaller brecciated areas have been observed in the surrounding district. None of them have been explored at depth, but they resemble breccia pipes on the surface. The pipe filling, however, generally contains angular fragments all of one rock type, and herein these small pipes differ importantly from the Braden Pipe. Commonly the breccia is strongly tourmalinized, and the tourmaline may contain a little chalcopyrite. These satellitic pipes seem to correspond in age to the pre-pipe breccia and would thus be products of some upward-acting force. They apparently were never subjected to the later pulsating and subsidence movements that affected the Braden Pipe.

Another minor, but interesting feature, presumably related to the Braden Pipe, is the presence of several pebble dikes, exposed mainly on 3 and 5 levels on the north side of the pipe. Not enough is known of them to be very specific about their attitudes and extent. In general, they vary in width from a few inches to not more than 5 feet. These pebble dikes contain well-rounded fragments, commonly bleached and in places mineralized by the main chalcopyrite stage. Spectacular specimens have been obtained from a pebble dike on the north edge of the pipe on 5 level where well-rounded bleached pebbles are set in a matrix of massive bornite.

### *Minor Structure*

Jointing and sheeting are well-developed in many parts of the district. A number of trends, albeit generally indistinct ones, can be recognized. Steeply dipping joints parallel to the northeast-striking set of faults and veins are common; a weaker complementary set follows a northwest trend.

Flat-lying sheeting is conspicuous in most of the older rocks—both extrusive and intrusive. At first it was thought that the sheeting reflected original flow bedding of the extrusive rocks. It now seems more likely that

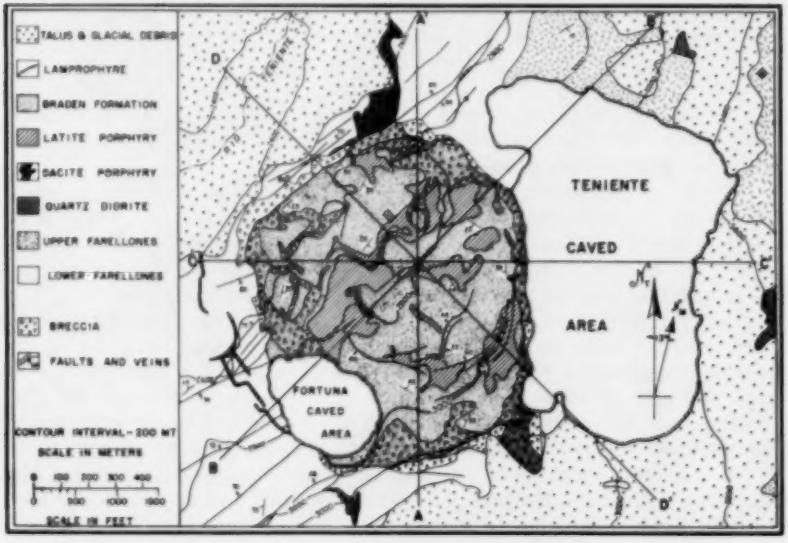


FIG. 5. Surface geology over the mine area.

most of it is sheeting in the restricted sense of the word, i.e. a near-surface feature with attitudes essentially parallel to either the present surface or an older one. The sheeting is not noticeably mineralized and therefore must be younger than the main period of copper mineralization.

## ECONOMIC GEOLOGY

Before proceeding, a brief summary of the nomenclature used at Braden may help the reader to visualize the orebody. Frequent reference to Figures 5, 6, 7, and 8 is also suggested.

Orebody dimensions are based upon an arbitrary cut-off of 1 percent of copper, but this figure does not necessarily determine mineable ore limits at Braden. Although the orebody has no consistent dip, the side nearest the pipe is called the hanging wall, and conversely, the side away from the pipe

is called the footwall. The principal mine levels and their respective elevations are:

| | | |
|---|---|---|
| H level | —9,973 feet— | Highest production level. Now caved. |
| F level | —9,646 feet— | Highest accessible level. |
| C level | —9,160 feet— | Highest level of current production. |
| 1 level | —8,619 feet— | Present main production level. |
| Sub-B level | —8,291 feet— | Lowest level of current production. |
| 5 level | —7,493 feet— | Lowest and main haulage level. |

### *Size, Shape, and Boundaries of Orebody*

In plan the orebody surrounds the Braden Pipe in a continuous ring that has a maximum width of about 2,000 feet. The widest part, which is on the east side on the upper levels, plunges counterclockwise around the pipe, so that on the lower levels, the orebody is widest on the north side. All current mine production comes from the wide portion on the east side of the pipe, called the Teniente area. Although the ore on the south and west sides is relatively narrow, a wide segment in the southwest quadrant, called the Fortuna orebody, was the source of all production between 1906 and 1922. On the west and northwest sides of the pipe, much of the upper part of the orebody has probably been removed by erosion.

The vertical extent of the orebody is still largely undetermined. Only two diamond drill holes have been drilled in the orebody below 5 level, and they show a maximum vertical dimension of at least 4,300 feet. The upper limit of the orebody is fixed by a leached capping of extremely variable thickness. On the average, the capping is between 100 and 400 feet thick, but in some places, good ore extends to the surface. On the other hand, in the breccias surrounding the pipe and in the andesitic flow breccias, leaching and oxidation penetrate downward a maximum distance of 1,150 feet below the surface.

Although the hanging wall roughly coincides with the edge of the pipe, the orebody is delineated by assay limits, not structural boundaries. Ore boundaries are all gradational, but the hanging wall is generally much sharper and more regular than the footwall. The hanging wall generally lies within the brecciated Braden formation, and its location depends upon the relative abundance of ore fragments in the breccia. The footwall traverses quartz diorite, fairly fresh andesite, and dacite porphyry and is fixed by the gradual diminution of random copper sulfide veinlets.

The host rock exerts an important influence upon the width and tenor of ore. Recognition of this relationship provides a useful aid in mine exploration. The best grade of ore is found in altered andesite or in andesitic flow breccia adjacent to the pre-pipe breccia. The geologic maps with their ore zone overlays also show that ore is most abundant in places where the host rock is both quartz diorite and andesite. This condition exists on the north, northeast, east, and southeast sides of the pipe; in other sectors the host rock is all andesite. The relationship between quartz diorite and ore is very real, but in detail, rather vague. One cannot say that quartz diorite, andesite,

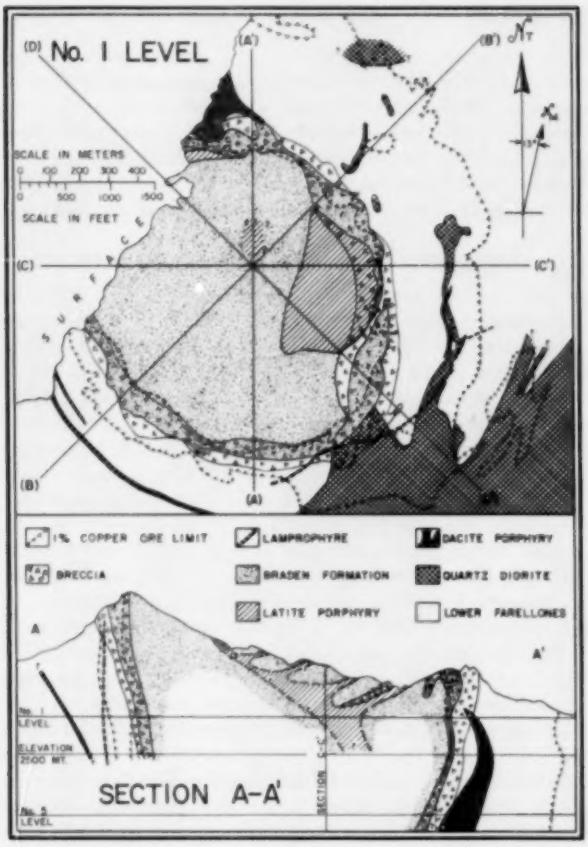


FIG. 6. No. 1 level plan and section A-A'.

or the contact between the two is a preferable locus for ore, but it can be stated that wherever quartz diorite and andesite occur together, the orebody shows a marked tendency to become wider and more irregular in outline (Fig. 6). It is the result of more intense fracturing, probably due either to the intrusion of quartz diorite or to geologic forces acting upon adjacent rock types of different rock competency.

Very little ore contains more than 5 percent of copper, and most of it is supergene ore already mined. The footwall and bottom limits of copper mineralization are extremely gradational so that there are immense tonnages of protore containing between 0.5 and 1.0 percent of copper. The current mill head assay averages 0.08 percent of molybdenite and 1.95 percent of copper, of which 0.22 percent is non-sulfide copper.

### *Rock Alteration*

In comparison with other porphyry copper deposits, hydrothermal rock alteration at Braden seems relatively mild. In general, the intensity and distribution of alteration reflect the net result of two superimposed stages.

The older alteration is apparently unrelated to the copper mineralization, as it appears to have been produced by intermittent quartz diorite intrusions emplaced at an earlier date. The result has been a spotty, locally-intense type of alteration that is much stronger in the older rocks than in the younger ones. The lower Farellones contains rather numerous irregular patches and masses of strongly argillized and/or sericitized rocks, and the member as a whole on the surface is typically iron-stained. The middle and upper

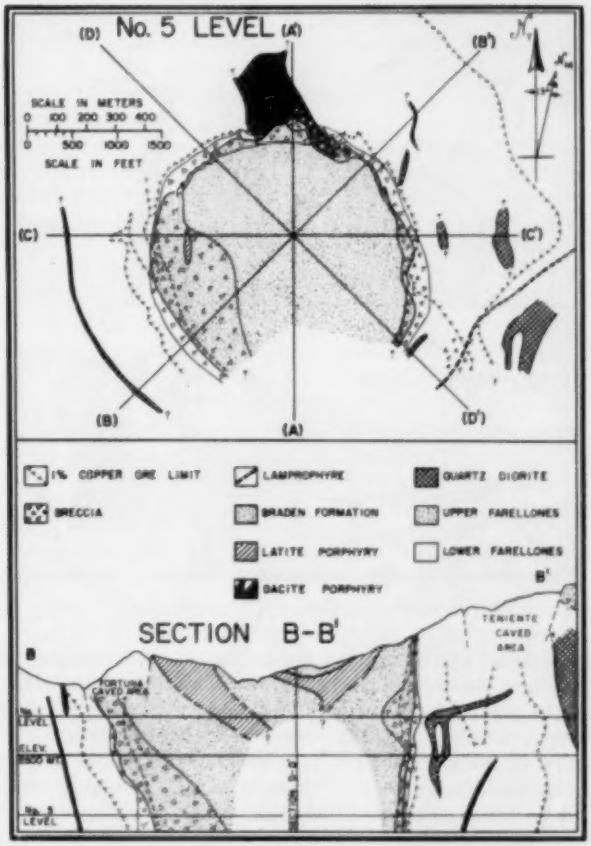


FIG. 7. No. 5 level plan and section B-B'.

members of the Farellones are much fresher and are altered or iron-stained only near quartz diorite intrusions or along veins and faults. Rock alteration of this type is common throughout the intrusive belt of central Chile.

A later alteration sequence forms a concentric pattern centered upon the Braden Pipe, with the alteration intensity gradually increasing toward the pipe. This period of alteration is directly related to copper mineralization.

Approaching the orebody from surrounding fresh rock, the first indication of the later period of hydrothermal alteration is a noticeable concentration

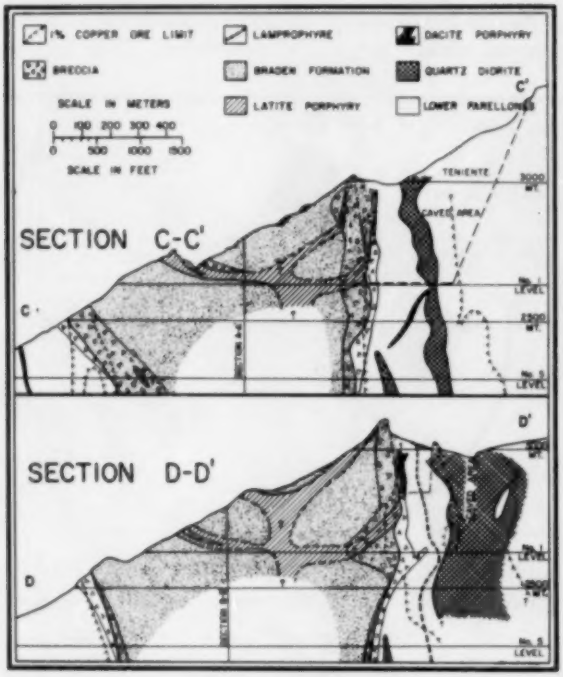


FIG. 8. Sections C-C′ and D-D′.

of basic elements about a mile from the orebody. This "basic front" is best developed north of the orebody and probably would have formed a continuous ring around the pipe had not intense alteration of the earlier period interfered with its development south of the orebody. This peripheral low-intensity alteration zone is characterized by abundant patches and veinlets of epidote, tourmaline, magnetite, and specular hematite in the volcanic rocks, commonly accompanied by minor amounts of calcite.

Next to the pipe, within a belt up to 3,000 feet wide that includes the orebody, both andesite and quartz diorite have been conspicuously and selec-

tively altered. The alteration provides a useful ore guide, for it serves to enlarge the ore target. The andesite is typically flooded with fine-grained secondary biotite that shows a slightly anomalous green color and is generally fresh, even where other rock-forming constituents are altered. The quartz diorite on the other hand appears to be silicified. Actually, however, there has been no appreciable addition of silica, but merely a breakdown of rock-forming minerals in which large amounts of free silica were liberated to form abundant secondary quartz. This was accompanied by almost complete destruction of original feldspars and ferromagnesian minerals so that the resultant rock is largely a fine-grained aggregate of sericite and secondary quartz. The selectivity of this alteration in affecting the two rock types so diversely is surprising. The different reactivity to the same altering media must be due to the coarser grain size and more acid composition of the quartz diorite compared with the andesite. This stage of alteration is earlier than the main period of copper mineralization, and it might be surmised that these changes occurred as mineralogic readjustments in response to the physico-chemical conditions that preceded ore deposition. It may possibly be related to intrusion of the dacite porphyry.

The pervasive argillic-sericitic-silicic sequence of alteration, so characteristic at other porphyry copper deposits, scarcely appears at Braden. In a few places, adjacent to the pipe, strongly altered andesite occurs, but more often fresh-looking biotitized andesite extends clear across the orebody to the pipe margin. There is, however, a moderate increase in alteration intensity toward the pipe. The relative scarcity of this typical porphyry copper alteration today does not necessarily mean that it never existed much more extensively at one time.

Several space-time relationships have been established that lead to interesting conjectures regarding the nature of the rock plug that originally occupied the Braden Pipe. The increase in alteration intensity toward the pipe is particularly significant, as well as the fact that the main periods of both alteration and copper mineralization are older than the pipe. Extrapolation of the alteration pattern suggests that rock formerly in the pipe was exposed to the most intensive alteration and may have consisted of a strongly silicified rock, or possibly a dacite porphyry intrusion, or both. This postulate has some additional supporting evidence. Generally the pre-pipe andesite breccia contains fragments that are moderately to strongly silicified, indicating that the present pipe margin may roughly coincide with a former outer limit of silicification. The Braden formation also contains a very large proportion of siliceous fragments in comparison with the amount of silicification outside the pipe. Moreover, the larger dacite masses are associated with strong silicification.

The widespread intermittent tourmalinization of breccias might be regarded as a late-stage type of alteration. The tourmaline was seemingly able to replace any rock type, starting with the smallest fragments in the matrix and proceeding to extreme cases where the entire breccia was replaced. Tourmalinization of breccia is always accompanied by strong bleaching of the fragments. The exact nature of the bleaching has not been studied,

but the strongly bleached fragments seem to be mostly aggregates of quartz and sericite.

### *Descriptive Mineralogy*

The minerals found in and close to the Braden orebody are described below in the order followed in Dana's "System of Mineralogy." The list, which includes ore, gangue, alteration, and secondary minerals, is not necessarily exhaustive, but it embraces all those that are abundant enough to have significance in the paragenetic history of the orebody.

*Gold* and *silver* are present in almost negligible quantities. The blister copper from Braden contains about 0.3 ounce of silver and 0.026 ounce of gold per metric ton. This trace of precious metals probably occurs in a late post-pipe mineralization associated with tennantite, galena, and sphalerite.

*Native copper* is fairly common in the lower part of the oxidized zone where it occurs with cuprite and limonite. It is found as wiry crystals in open spaces and as tabular plates in veins and fractures. It also occurs as irregular grains in cuprite that has replaced chalcocite.

*Stibnite* is reported from one of the northeast-striking quartz veins about 2 miles west-southwest of the orebody. According to notes made in 1921 when the vein was being mined for smelter flux, the stibnite occurs as needles in sulfide bands in the quartz vein. The sulfide bands contained mainly galena and sphalerite with minor pyrite and chalcopyrite. Some anhydrite was also present.

*Molybdenite* is scattered erratically throughout the orebody in a variety of occurrences, but it shows some affinity for pre-pipe breccia. Some specimen-type molybdenite occurs rather abundantly in quartz veins in and near the silicified dacite porphyry. More typically, it is found with other sulfides in random veinlets, especially those filled with quartz. It is apparently contemporaneous with quartz and occurs in flakes 1 to 10 mm in diameter that are concentrated along irregular marginal or central bands. Molybdenite was also deposited sparsely in the tourmalinized post-pipe breccia with chalcopyrite and pyrite in a quartz and anhydrite gangue. A fine-grained variety is found as films along some joints and fractures that are otherwise unmineralized. Molybdenite deposition seems to have been of relatively long duration.

Molybdenite is recovered as a by-product, but the recovery is very low. Metallurgical research work at Braden has recently suggested that the ore contains a high-rhenium variety of molybdenite that responds very poorly to flotation.

*Galena* is late in the paragenetic sequence and comparatively rare in the orebody. It is more abundant outside the mine area as a filling of the northeast-striking quartz veins, and occasionally it is found in commercial quantities. Mostly it is argentiferous, coarsely crystalline, and occurs with sphalerite, pyrite, chalcopyrite, quartz, and anhydrite.

*Chalcocite* has been the principal ore mineral and occurs both as a sparse primary mineral and as an abundant secondary mineral. The primary chalcocite has been found only on and below 5 level in the northern part of the

mine, where it shows an affinity for the dacite porphyry. It is generally with bornite, in which it forms irregular blebs and well-developed lattice-grating texture, suggesting that chalcocite and bornite were originally in solid solution. Under the microscope at high magnifications two varieties can be distinguished. The chalcocite is light gray and contains irregular patches of a somewhat darker and slightly bluish-gray mineral which is probably digenite, the isometric dimorph of chalcocite.

Secondary chalcocite is abundant above Sub-B level, where its deposition has approximately doubled the original tenor of the primary ore. It preferentially coats and replaces other sulfides in the order: bornite, chalcopyrite, pyrite. Supergene chalcocite is found as irregular masses where it has replaced sulfides in the breccias, as films on fractures in the massive sulfide veinlets, and as rims on disseminated sulfide grains. Complete replacement of sulfide veinlets by chalcocite is rare.

*Sphalerite* occurs in the same manner as galena in the northeast-striking set of veins. It is generally coarse-grained and ranges from a sub-metallic dark brownish-black to a resinous greenish-amber color.

*Covellite* is rare and occurs only as thin films on fractures in the primary copper sulfides, mainly in the upper part of the supergene zone.

*Bornite* seems to be entirely a primary mineral at Braden. It is moderately abundant, especially in the lower northern part of the orebody where it is one of the main ore minerals. Bornite is a common adjunct of the main stage of chalcopyrite deposition. It is also found in a later completely different mode of occurrence where cores of bornite up to an inch or more in diameter are enclosed in a shell of ankerite.

*Chalcopyrite* is the predominant primary copper mineral at Braden. In the upper part of the orebody, chalcopyrite is subordinate to pyrite, with which it is generally associated. The two minerals, however, are generally in separate grains.

Below Sub-B level, chalcopyrite is the predominant sulfide mineral. It is commonly associated, and in places intergrown, with bornite. In veinlets and patches, the chalcopyrite generally occupies an interior position relative to gangue minerals, but much of it is accompanied by little or no gangue. Chalcopyrite also occurs in the breccias as irregular patches and veinlets, generally with bornite and anhydrite. It was deposited throughout the whole paragenetic sequence.

*Pyrite* is the most abundant sulfide in the upper and southern part of the orebody. Between Sub-B and 5 levels it is subordinate to chalcopyrite, and below 5 level, pyrite appears to be almost absent. It occurs in veinlets and in openings in breccias, generally with a quartz gangue, and is more abundant toward the footwall. It is also found in the northeast-striking veins and in disseminated grains in altered areas throughout the district.

In form, pyrite is mostly massive and subhedral to anhedral. Small disseminated grains are generally rounded, but those larger than about 2 mm commonly show euhedral faces.

*Tennantite* is characteristic of the late post-pipe stage of mineralization and is found most commonly in the brecciated Braden formation along the

hanging wall. It occurs in well-formed tetrahedrons lining openings and fractures in the breccias with anhydrite, dolomite, or barite. Less commonly, it is massive in veinlets with bornite and chalcopyrite. Some specimens show a second generation of small tetrahedrons perched on top of older ones.

The chemical composition is variable and shows no apparent correlation with occurrence. Eleven samples varied between 91 percent tennantite and 62 percent tetrahedrite, with an average of 69 percent tennantite. The mineral is thus referred to herein as tennantite, although some of it is actually tetrahedrite. Compared with other copper sulfides, tennantite is relatively unimportant as an ore mineral.

*Enargite* is rare and occurs only in one part of the pipe where it seems to be related to a large mass of latite porphyry. It is found in the latite porphyry and in the nearby brecciated Braden formation as veinlets with pyrite and a little chalcopyrite in a quartz, anhydrite, or clay gangue. Assays show an average composition of 88 percent enargite and 12 percent famatinite. It tends to be coarsely crystalline and commonly shows striated faces. In polished sections, the mineral is pinkish, suggestive of the varietal species, luzonite.

*Quartz* is the most abundant gangue mineral and is found throughout the orebody and in the surrounding district with all types and stages of mineralization. It varies from very fine-grained milky quartz in some veinlets to large, clear, comb-quartz crystals lining open fractures and veins.

*Cuprite* is common in oxidized parts of the orebody where it replaces secondary chalcocite or fills cavities. It is generally massive and fine-grained, but felty masses of acicular crystals (chalcotrichite) are also found. An interesting occurrence is found on Sub-B level in the northern part of the mine where bright, lustrous cubes and octahedrons of cuprite are perched upon coarse flakes of molybdenite in quartz veins.

*Tenorite* occurs with malachite and azurite in a carbonate gangue as a minor oxidation product.

*Hematite*, in its specular form, is an abundant gangue mineral of the northeast-striking quartz veins. Fine-grained hematite is very common in the outlying "basic" alteration zone. It is found only sparsely in the orebody as medium-sized plates in some veinlets of the late stage mineralization.

*Magnetite* is an abundant accessory mineral in the volcanic and intrusive rocks of the area. It is concentrated in the "basic" alteration zone and forms readily from the breakdown of rock-forming ferro magnesian minerals. There are a few areas in the orebody where magnetite occurs in veinlets and small irregular masses, but generally it is much rarer than in the surrounding fresh rocks.

*Limonite* occurs on the surface and throughout the oxidized zone as stains, crusts, and coatings after sulfides. It is presently being deposited in mine openings.

*Calcite* is rather abundant as a fine-grained alteration product. It is rarely seen in hand specimens, but under the microscope it very commonly

appears with sericite as an alteration of plagioclase feldspar. It also occurs in the matrix of the Braden formation.

*Ankerite* and *Rhodochrosite* are gangue minerals characteristic of the late-stage tennantite mineralization. Ankerite is also fairly common as a shell around disseminated bornite grains. Rhodochrosite is rare.

*Malachite* and *Azurite* are locally abundant in the upper part of the oxidized zone and in the breccias surrounding the pipe. They seem to be oxidation products of the late tennantite-carbonate mineralization. Malachite is the more abundant and lines cavities and fractures as botryoidal or fibrous masses.

*Epidote* appears to be completely lacking in the orebody but is very abundant in the outlying "basic" alteration zone. It is also an important accessory mineral in the volcanic rocks where it commonly forms amygdules in the vesicular flows.

*Tourmaline* seems to be characteristic of the Andean metallogenic province and is found extensively in and around the Braden orebody. The most typical occurrence is as very-fine-grained aggregates of tiny black needles replacing the matrix of breccias. Where it has formed in cavities and open fractures, the tourmaline is coarser and forms rosettes and clusters of needles.

*Sericite* is probably the most abundant alteration product of the intensely altered rocks. Quartz and sulfides are generally the only attendant minerals in the altered quartz diorite. Sericite is also found in thin bleached borders along sulfide veinlets in the andesite where it is an alteration of the secondary biotite. Local patches of strong sericitic alteration well outside the orebody are apparently related to earlier dioritic intrusions.

*Biotite* is particularly plentiful as the fine-grained secondary type already mentioned under *Rock Alteration*. It is generally in small lathy crystals scattered through the groundmass of the andesite, and more rarely, in the plagioclase phenocrysts. This biotite is moderately pleochroic, grassy green in color, and in places so abundant as to constitute more than half the rock. A later generation of biotite occurs sparsely as larger, brownish flakes along the margins, and at intersections, of some sulfide veinlets with quartz-anhydrite gangue.

*Chlorite* is most important as an alteration product of secondary biotite and of the hornblende and biotite phenocrysts in the quartz diorite and dacite porphyry. Most of the fresher rocks outside the mine area also contain some chlorite as a result of mild propylitic alteration. It is also sparse to abundant in sulfide veinlets of the main stage of mineralization.

*Clay minerals*, resulting from pervasive argillic alteration, are sparse at Braden compared with other porphyry copper deposits. Thin-sections show traces of clay minerals, but none in quantity. Two types, however, are moderately abundant as the filling in recent fractures and in voids of flow breccias. Massive white *halloysite* has been found on the surface in veins and faults throughout the district. Another clay mineral, found within the mine, especially in vugs and cavities in the andesite flow breccia, has been tentatively identified as *viterbite*, a phosphate-bearing allophane, intermediate between evansite and allophane. The material is soft, and its color, which

ranges from white to apple-green, seems to be a function of its content of adsorbed copper. Structurally, it is amorphous (5); the refractive index is about 1.482. The Braden Copper Company Chemical Department has analyzed a sample of the greenish material as follows:

| | | |
|---|---|---|
| CuO—8.24% | $Al_2O_3$—31.66% | $P_2O_5$—29.41% |
| $SiO_2$—13.88% | $H_2O$—16.76 | |

The origin of this clay is not clear, but it seems to be a product of post-ore alteration of some other mineral that originally occupied the voids in the flow breccia. It may have been a glass, but the high phosphate content is difficult to explain.

*Chrysocolla* occurs uncommonly in the upper part of the oxidized zone as a coating on fractures, some of which have not previously been mineralized.

*Leucoxene* is common in andesite and quartz diorite throughout the district as an alteration of rutile, ilmenite, or titaniferous magnetite.

*Chalcophyllite* is found locally as an oxidation product of tennantite. Some of it is of specimen quality and consists of lustrous green hexagonal plates generally admixed with malachite and azurite.

*Barite* is encountered occasionally in the anhydrite-carbonate gangue of tennantite mineralization. More frequently, it is seen as a coarse-grained filling in some of the northeast-striking quartz veins.

*Anhydrite*, like tourmaline, seems to be another mineral that is typical and distinctive of the Braden orebody. It is very common as a gangue mineral, being second only to quartz in abundance. In some parts of the mine, particularly on the lower levels, small disseminated grains and patches of anhydrite are scattered throughout the groundmass of all the rocks except the lamprophyre. It is more noticeable, however, as a coarse-grained gangue mineral in veinlets and breccias, where it often exhibits a characteristic pinkish-violet color.

*Brochantite* is found only in one area of oxidized mineralized breccia in the northern part of 1 level where it forms a conspicuous coating on cuprite.

*Gypsum* is nearly as abundant as anhydrite. Virtually all of it has been formed by the alteration of anhydrite, but at least one example of primary gypsum has been noted. An unusual occurrence is a mass of solid gypsum about 40 feet in diameter in the brecciated Braden formation. It contains large, clear selenite crystals up to 4 feet in length.

*Chalcanthite* is being deposited in some of the mine workings by water percolating downward from the caved ground on the surface.

*Huebnerite*, in small subhedral grains with quartz, is a rare constituent of the tennantite mineralization.

*Ferrimolybdite*, as an alteration of molybdenite, is seen very sparsely in some of the oxidized ore.

Lindgren and Bastin (1) also mention kaolin, melanterite, copper pitch ore, epsomite, and a sky-blue basic aluminous sulfate of copper. None of them was identified during the recent study.

### *Mineral Paragenesis*

A paragenesis of the most important minerals at Braden in relation to the major geologic events is shown schematically in Figure 9. Most of the minerals are commonplace, but are of interest in that we can establish the paragenetic sequence with enough precision to show the progressive changes that took place in the ore-forming solutions (the term *solution* is used in its broadest sense herein). The initial solution must have been rich in copper, iron, sulfur, calcium, and silica, with minor molybdenum. Deposition of these components was very rapid at first, but diminished rather abruptly and then continued in a small way for the remainder of the period of mineralization.

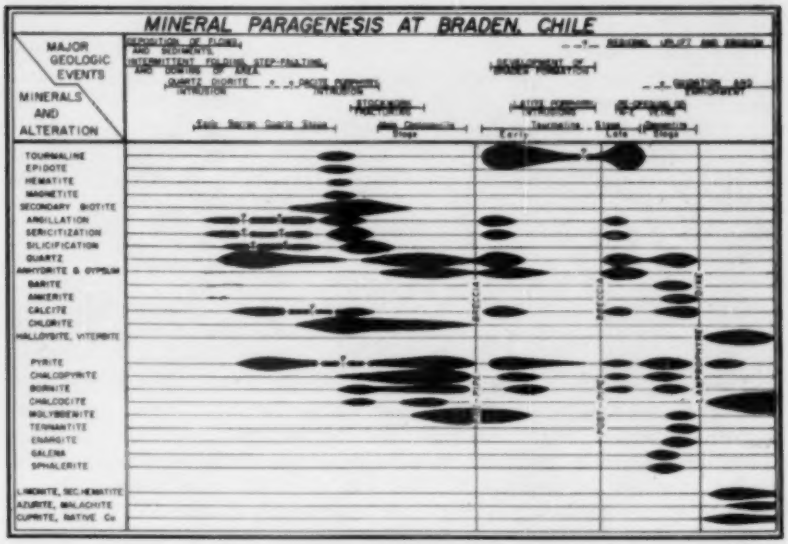


FIG. 9. Mineral paragenesis chart.

Near the middle of the sequence, boron was introduced in large quantities as tourmaline, but the deposition of tourmaline ceased just as abruptly as it had started. Toward the end of the sequence, lead and zinc were deposited as simple sulfides. At the close of mineralization, arsenic and antimony attained concentrations sufficient to deposit copper sulfosalts; barium, manganese, and the carbonate radical appeared simultaneously in the gangue.

Based upon diagnostic assemblages of hypogene minerals and upon different modes of occurrence, five stages of mineralization, each named after its most distinctive mineral, have been recognized. Although mineralization is described according to stages, it is more likely that it took place in one nearly continuous sequence, in which intervening structural events evoked changes in the composition and physical chemistry of the mineralizing solutions.

*Early Barren Quartz Stage.*—Of relative unimportance is an early period of quartz deposition in the northeast-striking faults. It apparently took place during the hiatus between deposition of the lower and middle members of the Farellones formation. The only adjunct of the quartz seems to have been a little pyrite. Most vein filling of the early barren quartz stage has been shattered and granulated by later movement on these veins.

*Main Chalcopyrite Stage.*—If mineralization at Braden had never proceeded beyond the second, or main chalcopyrite, stage, the orebody today would not differ much in size or tenor. The bulk of the sulfides was introduced during this stage into a random network of veinlets, forming a stockwork of low-grade ore. At Braden, as at most other porphyry copper deposits, the term "disseminated copper" cannot be applied in a strict sense, for at least 90 percent of the hypogene sulfides occur as obvious fracture-fillings.

The grade of ore is essentially proportional to the degree of stockwork fracturing, which increases gradually from footwall to hanging wall. Individual veinlets are not persistent, and they either die out within a few feet or join into other veinlets. Average width is between 1/64 and 1/4 of an inch. They may show offsetting relationships in which the widest veinlets commonly produce the largest displacements. Veinlets throughout the orebody give a general impression of randomness, but statistical analyses by equal area stereographic projections shows a somewhat higher frequency of veinlets that strike tangent to the Braden Pipe and have an average dip of 48 degrees toward it.

As shown in the paragenetic chart (Fig. 9), stockwork fracturing presumably continued for some time after the main chalcopyrite stage had started. The cause of the fracturing is an intriguing subject for speculation. Indirect evidence suggests that fracturing, like alteration, is related to a hypothetical intrusive center which formerly occupied the Braden Pipe. The increase in fracturing intensity toward the pipe, and the fact that abundant rock fragments, mineralized by the main chalcopyrite stage, are found throughout the Braden formation substantiate this thesis in space and time, respectively.

Although the stockwork veinlets vary considerably in mineralogy, attempts to classify them mineralogically have been futile. Any subdivision on this basis would be artificial and very local. Within several feet, an individual veinlet can, and commonly does, contain all of the principal minerals of the chalcopyrite stage. The sulfides characteristic of this stage are chalcopyrite, pyrite, bornite, molybdenite, and primary chalcocite in a gangue of quartz, anhydrite, and chlorite. The minerals occur individually or in almost any combination with other sulfide or gangue minerals, except for the chalcocite, which always occurs with the bornite. Most of the veinlets appear to be clear-cut fracture-fillings and commonly show banding. Some of the narrow ones, however, seem to entail spotty replacement along hair-line fractures, in which case the groundmass was more susceptible to replacement than the phenocrysts. Veinlets of the main chalcopyrite stage generally have narrow bleached margins in the andesite, caused by the alteration of secondary biotite to chlorite and/or sericite.

Mineralization of this stage occurs somewhat differently in dacite porphyry

than in the other rocks. There seems to be a much larger proportion of sulfide grains, particularly bornite, that are actually disseminated in the dacite porphyry than in the andesite or quartz diorite. Some of these disseminated sulfides may actually be syngenetic, so that the dacite porphyry would be contemporaneous with at least the first part of the main chalcopyrite stage.

*Early Tourmaline Stage.*—Much of the mineralization that followed the main chalcopyrite stage was deposited, along with plentiful tourmaline, in breccias. The first locus of deposition was in the pre-pipe breccia surrounding the pipe, and to a much lesser extent, in small satellitic pipes in the out-

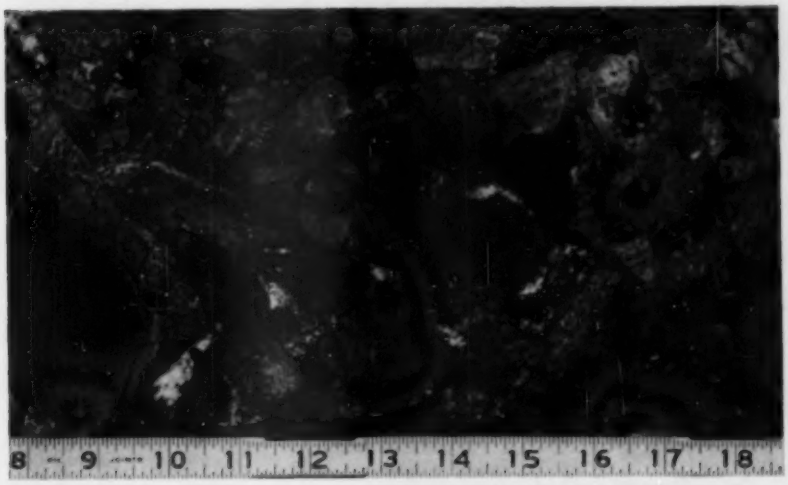


FIG. 10. Photograph of pre-pipe breccia showing partially bleached (propylitized) andesite fragments in tourmaline-chalcopyrite matrix.

lying region. The same type of mineralization is also found in the orebody in a few persistent braided stringers of breccia that are radial to the pipe and dip vertically.

The early tourmaline stage is characterized by a gangue of tourmaline, quartz, and anhydrite, containing chalcopyrite, with lesser bornite and pyrite. Chalcopyrite and tourmaline are by far the most abundant and occur typically together as fillings and replacements in the matrix of brecciated andesite (Fig. 10). Molybdenite is locally important and is the earliest sulfide of this stage; tourmaline is clearly the earliest gangue mineral. In most places, this tourmaline-rich assemblage is accompanied by moderate bleaching of the breccia fragments.

The early tourmaline stage mineralization replaces the matrix of pre-pipe breccia, in which are found fragments of rock well-mineralized by the main chalcopyrite stage, and mineralized fragments of pre-pipe breccia are found plentifully in the Braden formation. Thus the early tourmaline stage is later than the main chalcopyrite stage and earlier than the Braden formation.

*Late Tourmaline Stage.*—Except for a much greater proportion of tourmaline and the lack of molybdenite, the late tourmaline stage is mineralogically much like the preceding early tourmaline stage. However, it is found only in the post-pipe breccia in the Braden formation. Rock fragments in the tourmalinized post-pipe breccia are almost invariably strongly altered to sericite and/or clay minerals.

*Tennantite Stage.*—The tennantite stage is a distinctive late-stage mineralization that reflects decreasing pressure and temperature as metallization waned. Its favorite abode seems to be in open spaces in the post-pipe breccia formed by final subsidence of the pipe-filling material.

Tennantite, galena, and sphalerite are the typical sulfides; carbonates the typical gangue. The carbonate is mostly ankerite, but calcite and rhodochrosite are also present. This distinctive assemblage is accompanied by any one or several of the following minerals: pyrite, chalcopyrite, bornite, molybdenite, quartz, anhydrite, gypsum, barite, specularite, and viterbite (?). Galena, sphalerite, and anhydrite commonly occur together and are earlier than a later suite comprised of tennantite, bornite, and ankerite. The tennantite occurs in places as small but rich pods of massive ore in the post-pipe breccia. The largest yet found was more or less spherical in shape, with a diameter of about 200 feet. It is reported to have averaged between 20 and 30 percent of copper.

A somewhat different phase of the tennantite stage is represented by sparse veinlets of enargite, pyrite, and chalcopyrite with a gangue of quartz and anhydrite in and near the large latite mass exposed on 1 level. Its relation to the tennantite mineralization is uncertain, but the enargite is probably earlier than the tennantite.

### *Mineral Zoning*

In addition to the concentric zonal pattern of the several alteration stages at Braden, the hypogene sulfides also demonstrate a well-defined zoning.

On a district-wide scale, a roughly elliptical area extending from about half a mile southwest of the pipe to 2½ miles northeast of the pipe seems to represent a central "hot-spot" of copper mineralization. Surrounding this core, veins are more likely to contain a lower temperature assemblage of sulfides such as galena and sphalerite, or even stibnite.

Within the mine area, both lateral and vertical zoning can be recognized. From the hanging wall outward toward the footwall, chalcopyrite decreases markedly, whereas pyrite appears to become somewhat more plentiful. Thus the outer limit of ore is a function of mineralogy as well as intensity of stockwork fracturing.

On the north and northeast sides of the pipe, where we have some information from below 5 level, pyrite gradually decreases downward and virtually disappears at about the elevation of 5 level. This downward diminution of pyrite is accompanied by a corresponding increase in bornite so that ore from below 5 level consists essentially of clean chalcopyrite and bornite in about equal amounts. Below the elevation where pyrite disappears, sparse primary chalcocite is found.

### *Oxidation and Secondary Enrichment*

Outcrops over the main Teniente and Fortuna orebodies have long since been destroyed by subsidence. The only record of these exposures is a brief description by Lindgren (6) in which he states: "The normal outcrop is dark reddish-brown, the rock being seamed in all directions with rusty limonite, and there is often not a sign of copper over large areas right above the ore. There are copper stains in places, mostly chrysocolla. . . ."

In other sectors, where the orebody is thinner and of lower grade, surface outcrops are still intact. Over the unmined part of the orebody on the south side of the pipe, no copper minerals are found on the surface. The rock is a weathered, light to medium gray andesite, crisscrossed by closely-spaced, thin fractures containing rusty-brown to yellowish limonite and some quartz-tourmaline veinlets. Rarely the fractures contain a little pyrite. Shallow prospects in this area often encounter fresh sulfides within 10 feet of the surface.

Over the unmined northern portion of the orebody, the andesite is commonly fresh-looking at the surface, although most veinlets have been oxidized and leached. Fresh sulfides can often be found and include pyrite, generally with some secondary chalcocite, and also a little molybdenite. Recent fractures in the outcrops are commonly coated with chrysocolla. Such diversity in the appearance of outcrops over the orebody can probably be attributed to recent glaciation.

The depth of oxidation at Braden is extremely variable and depends upon three factors: topography, rock type, and structure. Structure is much more effective than the other two. Oxidation is deepest in the andesite flow breccias where it attains a maximum depth of 1,150 feet below the surface on the northeast side of the pipe. It also extends much deeper in the breccias along the hanging wall than in the relatively unbroken rock of the footwall. Average depth of oxidation along the hanging wall is about 500 feet, whereas in the footwall area, sulfide ore may extend to within a few feet of the surface. The boundary of oxidation is generally gradational, but in places, especially where breccias are involved, it is very sharp, with the transition between complete leaching and good grade sulfide ore taking place within ten feet. The deeper oxidation may penetrate downward well into the zone of supergene enrichment, thereby confirming a fairly recent uplift of the district.

Mineralogically, the oxidized zone is relatively simple, with a low average copper content not exceeding 0.25 percent. Rusty, yellow-brown limonite is the characteristic and most abundant product of oxidation. Near the surface, chrysocolla, malachite, and azurite are the predominant copper minerals; cuprite is more typical of oxidation penetrating downward into the supergene zone, and native copper extends even deeper, generally to just above the bottom limit of oxidation. Ores of the tennantite stage, upon oxidation, yield a different and very distinctive suite of minerals. Partially oxidized remnants of tennantite ore are typically rimmed with azurite, which is coated with malachite, which in turn has a coating of chalcophyllite flakes. Where massive chalcocite has been oxidized, it commonly goes to cuprite containing

tiny disseminated grains of native copper, both coated, in some places, with brochantite.

The zone of supergene enrichment is thickest beneath the highest outcrops on the east and south sides of the Braden Pipe. Toward the northwest, where the Teniente Canyon has cut deeply into the orebody, the supergene zone decreases in thickness and almost disappears beneath the canyon. As might be expected, the supergene sulfide zone extends deepest beneath or near where oxidation has been most extensive. For the Teniente part of the orebody as a whole, important secondary enrichment stops at about Sub-B level, some 1,700 feet below the surface, although traces of secondary chalcocite have been found well below 5 level. Enrichment is generally greatest at the top of the supergene zone and gradually diminishes downward. Mineralogy of the supergene zone is simple, consisting of all types of primary ore minerals and pyrite coated or replaced in varying degrees by chalcocite. The chalcocite is massive and shows both a dull or bright luster; sooty chalcocite is rare.

## GEOLOGIC HISTORY OF THE OREBODY

Interpretation of the available evidence indicates a mode of origin for the Braden orebody quite different from the one now recorded in geologic literature. Some parts of the story are still inscrutable and require additional detailed study; other parts seem to be well-established. Eventually, as exploration and mining penetrate deeper into the orebody, and especially as the Braden Pipe becomes more thoroughly delineated and better understood, mining geologists will have a unique and unexcelled opportunity to probe and examine the very roots of a large metallic orebody. The recent establishment of a resident Geology Department at Sewell will insure against any forfeiture of this opportunity.

In summary, all of the individual events described separately in the preceding sections are integrated below into a geologic history of the orebody.

The earliest recognizable event in the Braden Mine area was the deposition of massive andesitic flows of the lower Farellones formation just after the hiatus that marked the close of the Mesozoic Era. The fact that these rocks are younger than the upper Cretaceous Chilense formation is the only tie that we have with the geologic time scale.

Even at this early stage, the long chain of events leading up to copper mineralization had already commenced with a doming of the volcanics and development of the strong northeast-striking quartz veins, presumably due to an early period of quartz diorite intrusion. The lower Farellones member was folded, somewhat fractured, and locally altered at this time, and subsequently exposed to erosion. There followed a short period of renewed volcanic activity, and the middle member of the Farellones formation, with its interbedded volcanic flows and terrestrial sediments, was deposited, accompanied by frequent tilting of the terrain. Most of this member was completely removed by another period of erosion. There was also some additional displacement along the northeast-striking veins and faults. During a

final period of volcanism, the thick and varied beds of the upper Farellones member were deposited on top of all the older rocks. Subsequent folding and tilting have been almost negligible in the Sewell area. Intrusion of different facies of the quartz diorite magma, as apophyses of the underlying Andean Batholith, seems to have continued intermittently, with attendant uplift and normal faulting, throughout all of Farellones time.

At this point, the stage had been set for hypogene mineralization, which at Braden apparently followed the familiar pattern of hydrothermal emplacement, characteristic of many other porphyry copper deposits. The dacite porphyry, or its parental late-stage acid fraction of the Andean Batholith magma, is the ostensible prime source of mineralization. We can surmise that a large mass of dacite magma, perhaps as a cupola of the Andean Batholith, invaded at least a part of the space now occupied by the Braden Pipe. It spread dike-like for a short distance to both the north and south of the main stock and formed a crude conesheet. Emanating from this intrusive center, well in advance of the magma, were hydrothermal solutions that effected profound changes in the surrounding rocks. Nearest the stock, there probably was formed a shell of strong silicification in both the dacite itself and the adjacent rocks. Just outside the silicified zone there may have also been a thin concentric shell of strong sericitic and/or argillic alteration in both the quartz diorite and the andesite. As a result of the high intensity alteration nearest the stock, basic elements, including iron, calcium, potassium, and some aluminum, were released from rock-forming minerals and migrated outward. Some of the iron and calcium traveled more than a mile to form abundant epidote, hematite, magnetite, tourmaline, and a little calcite in the outermost alteration zone. The other bases, along with some of the iron, were not as mobile, and deposited as abundant secondary biotite in the andesite closer to the stock. Quartz diorite in the same area, with its coarser grain size and more acid composition, reacted differently than the andesite and broke down into a fine-grained aggregate of sericite and secondary quartz.

This mass of diversely altered rock, circular in plan, and possessing a wide variety of structural properties, was then subjected to geologic stresses that broke and closely shattered a large block of ground surrounding, and possibly including, the hypothetical dacite porphyry stock. The cause of this stockwork fracturing is not clear, but the fact that fracturing intensity is almost inversely proportional to its distance from the stock suggests that it must also be somehow related to the stock. Indeed, the stock itself and the surrounding rocks that formerly occupied the pipe were possibly shattered, or perhaps even brecciated at this time. The partial retreat or withdrawal of magma from beneath the dacite stock seems to offer one of the most plausible explanations for this intense and concentrated fracturing.

The first, or main chalcopyrite stage, filled the stockwork fractures while fracturing was still continuing. At depth, chalcopyrite and bornite, with minor molybdenite and primary chalcocite, all in a gangue of quartz and anhydrite, were the principal fracture fillings. Nearer the surface, presumably in an environment of lower temperature and pressure, pyrite and chalcopyrite prevailed in place of bornite. A similar change took place from hanging

wall to footwall. Some of the earliest chalcopyrite and bornite may have been syngenetic in the last of the dacite porphyry.

The main chalcopyrite stage closed with a structural cataclysm that was the precursor of the Braden Pipe as it appears today. Although our knowledge of the nature and origin of this structural event is very meager, we know that it succeeded in breaking loose the plug of rock within the pipe, and in so doing, it formed the pre-pipe breccia. This phenomenon, which presumably lowered prevailing temperatures and pressures appears to have promoted the deposition of abundant tourmaline. The same sulfides as before were deposited along with the tourmaline, but in much smaller amounts. Some spectacular tourmalinized and mineralized breccias were formed extensively in the andesite (Fig. 10) and quartz diorite around the margins of the Braden Pipe at this time.

The next recognizable event in the orebody's history was the evolution of the Braden formation. The very nature of this rock, with its anomalous rounding of fragments, abundance of ore fragments, and great vertical extent, bespeaks an origin comprised of uncommon geologic circumstances. The close time and spatial correlation between the Braden formation and the latite porphyry provides a clue.

Intermittent intrusion of latite porphyry is almost contemporaneous with the period in which the Braden formation developed. It does not seem improbable that a pulsation of the latitic magma within a conduit underlying the Braden Pipe may account for some of the anomalous features of the Braden formation. The high proportion of silicified and mineralized fragments further suggests that the original rock plug was never completely ejected from the pipe, leaving a gaping hole in the crust as supposed by Lindgren and Bastin (1). Moreover, the scarcity and small extent of bedding, combined with the extreme freshness of most sulfides in the Braden formation, belies the former existence of any extensive crater lake. Rather, it seems that renewed upward-acting forces beneath an existing stock dislodged and perhaps further shattered both the stock and some of the adjacent altered and mineralized ground. The actual breaking-loose would have taken place along a locus on the outer edge of the strong silicification. The injection of several different facies of latite porphyry may coincide with upward and downward displacements of rock within the pipe. During times of subsidence, a shallow lake may have developed at the surface, giving rise to a crude bedding in some portions of the Braden formation. The final phase, after the last intrusion of latite porphyry, was a period of substantial subsidence. Mineralization seems to have resumed almost at once, with deposition confined largely within the brecciated Braden formation. The ore-forming solutions had apparently changed very little, for, with the exception of molybdenite, they deposited the same tourmaline-rich assemblage of minerals as before, but only in smaller amounts. There followed a period, probably of short duration, in which there was renewed opening of the northeast-striking veins and possibly some additional subsidence of material within the pipe. This final structural activity coincided with the last stage of hypogene mineralization in which a group of relatively low-temperature minerals was deposited sparingly in the

northeast-striking veins and in the brecciated Braden formation. These minerals are also found in tiny persistent veinlets in parts of the unbrecciated Braden formation. Tennantite, sphalerite, and galena, in a carbonate gangue, are typical of this stage, and all minerals of the previous stage, with the notable exception of tourmaline, are present too, but in small quantities. A little coarse-grained molybdenite reappears in this final stage.

Emplacement of a narrow discontinuous lamprophyre dike, glaciation, supergene enrichment, and erosion complete the geological biography of the Braden orebody.

## COMPARISON WITH OTHER DEPOSITS

The last description of the Braden orebody, prepared more than 40 years ago, portrays a genesis more or less unique among orebodies. Braden seemed to have very little in common with other porphyry copper deposits. Conclusions derived from the recent study, however, indicate that in many ways, including its origin, the Braden orebody is almost a model porphyry copper deposit. From comparisons between Braden and other porphyry copper districts, we can draw some interesting inferences about the mechanics of porphyry-type ore deposition in general.

The Braden orebody clearly belongs to the Andean clan of the porphyry copper deposits. It possesses many features that individually are common to other porphyry coppers, but in its entirety, it is unique. The interrelationship of intrusive activity, breccia pipe formation, hydrothermal rock alteration, and metallization is especially well illustrated at Braden.

Mineralogically, mainly by virtue of its abundant tourmaline, Braden most resembles the other Andean porphyry coppers—Disputada, Rio Blanco, and El Salvador in Chile, and Toquepala, Quellaveco, Cuajone, and Cerro Verde in southern Peru. The similarity between Braden and Toquepala, as pointed out by Richard and Courtright (*7*), is especially striking.

The metallic minerals are not particularly distinctive, but hypogene anhydrite or gypsum, in such prodigious amounts as a gangue mineral, is unusual and apparently has no parallel among other porphyry type deposits. A possible clue to its abundance at Braden is the position of thick gypsum beds in a portion of the stratigraphic column that would normally underly the orebody.

The Braden deposit demonstrates rather well a relationship between mineralization and intrusive sequence that is characteristic of many ore deposits. Typically, the intrusive rocks become increasingly more acid, with mineralization occurring at or near the height of acidity, and then generally followed by a small post-mineral intrusion of basic composition. At Braden, the sequence is: diorite, quartz diorite, dacite porphyry, latite porphyry, and hornblende lamprophyre, with mineralization extending from the end of the dacite to the end of the latite. At Toquepala, the sequence is similar; diorite, dacite porphyry, and latite porphyry, with ore deposition between the dacite and latite. Porphyritic textures prevail in the more acid rocks. The senior author has observed comparable successions in other Andean-type deposits, at many of the copper deposits in the southwestern United States, at Climax,

Colorado, and even in a simplified manner in the Coeur d'Alene District of northern Idaho. This is not to imply that all orebodies follow this same pattern, but only to suggest a feature that might be common at least to the porphyry-type deposits and prevalent enough to be useful as an ore guide.

Within the past two decades, rock alteration at most of the large porphyry copper mines has been described in considerable detail, and a common prototype has been recognized. Although rocks at Braden seem to be comparatively fresh, rock alteration probably did not deviate much from the standard. There appears to be a good possibility that the most strongly altered rocks have been disrupted and destroyed by the Braden Pipe. Chemical changes within the rocks at Braden also seem to fit the normal pattern of porphyry-type rock alteration. Analyses of fresh and altered rocks substantiate the recent view that hydrothermal alteration involves no important addition or subtraction of material but merely entails a rearrangement of existing components. Secondary biotite, in the quantity found at Braden, is unusual, but it is also common at Bingham, Utah and in the andesite at El Salvador, Chile. The breakdown of diorite into an aggregate of sericite and secondary quartz, exactly like that at Braden, has been noted in many places, particularly at Toquepala (*7*).

Structurally, the porphyry copper deposits exhibit some express similarities, and Braden has one or more features in common with all of them. An almost universal trait, especially well-developed at Braden, is the circular configuration of alteration, mineralization, and structural elements, arrayed concentrically around a common center. Orebodies in which this pattern of centrality is most perfectly developed commonly have barren cores for one reason or another. Climax, Santa Rita, Toquepala, and Braden are good examples of this barren-core type in which the orebodies in plan are ring-shaped. In others with a well-developed concentric pattern, the orebody itself occupies the central area, forming orebodies such as Bingham, Butte, and Morenci. Most of the mineralized breccia pipe deposits belong to this group, although, strictly speaking, many of them cannot be classified as porphyry coppers. Another large group includes deposits such as Ajo, San Manuel, and El Salvador where the concentric pattern is only imperfectly developed, resulting in orebodies that are arcuate or crescent-shaped. A fourth subdivision embraces orebodies like Chuquicamata, Ray, and Miami-Inspiration where mineralization seems more closely allied with lineal elements such as major faults and shear zones.

On the west coast of South America, and perhaps in other regions too, the study of porphyry copper deposits seems to be almost synonymous with the study of breccia pipes. In this respect, Braden has another common bond with many other porphyry copper deposits. Although no actual breccia pipes have been found in some of the porphyry copper districts, nearly all of them display at least some closely allied phenomena such as pebble dikes, small to large diatremes, or unexplained and unclassified breccias. In many of these occurrences the fragments are rounded and there is good evidence of vertical displacement, both upward and downward. Smythe (*8*) has noted the prevalence of pebble dikes and breccias at Chino, Ray, and Ruth. He

reports the interesting occurrence of large fragments of the basement complex in pebble dikes at Ruth in an area where the basement rocks are nowhere exposed.

Pebble dikes and breccia pipes are not confined to porphyry copper districts, but are found with other base metals and with uranium deposits; even the kimberlite pipes may be distant relatives. Many of them are barren, and their origins still are not thoroughly understood. Braden probably provides as good an explanation as any for the evolution of breccia pipes. Here, the recurrent advance and retreat of a magma within a conduit at the cupola of a batholith seems to have been the most likely means of breccia pipe formation.

This depiction substantiates at least two other postulates of ore deposition. The first, pointed out many years ago by B. S. Butler (9), is the important kinship between metallic orebodies and the late fractionated portion of a magma that collects in the cupolas of a batholith. This relationship gives us an extremely helpful ore guide. In the Chilean portion of the Andean Cordillera, for example, the numerous occurrences of diorite are, in themselves, of no real significance, but the mining geologist who failed to investigate carefully a dacite or latite intrusion would indeed be negligent.

The second postulate is the less well-supported notion that many mining districts have an early history of some concentrated upward-acting force, followed by later relaxation and subsidence. The Braden Mine area seems to have undergone a structural cycle of this nature, and the senior author has observed a similar sequence in the Santa Rita District of New Mexico. There are indications that a comparable cycle may have been operative in other porphyry copper districts.

At Braden, the interrelationships of hydrothermal alteration, stockwork fracturing, metallization, and brecciation are so clearly demonstrated that they may possibly be able to shed some new light on the enigmatic process of ore deposition. Moreover, the evidence at Braden seems to substantiate previous studies by the senior author at Climax, Colorado and Santa Rita, New Mexico that point to a fundamental difference between vein deposits and porphyry-type orebodies.

Ever since the commendable alteration studies at Boulder County, Colorado (10), Butte (11), and Tintic (12), mining geologists have attempted to reconcile the classic picture of rock alteration surrounding veins with the pervasive, often ill-defined type of rock alteration that accompanies porphyry-type deposits. These attempts have invariably been unsuccessful.

In veins, the altering solutions are guided by distinct individual channels along which they react with the wallrock. This same channelway affords ingress for the metallizing solutions and serves as a locus for ore deposition. The result is an ore shoot enveloped within an alteration halo, in which the rocks nearest the ore have undergone the highest intensity of rock alteration. This vein-forming process is generally relatively deep-seated, and the igneous source rock may be remote.

In porphyry-type deposits, the picture is quite different. Butler (13) has pointed out the structural contrasts between the two types. In porphyry deposits the parent intrusive is generally close at hand, widespread stockwork

fracturing is the dominant feature, and mineralization occurs at relatively shallow depths. Altering solutions emanating from an intrusive source are not confined to one or even several channelways, but spread outward, pervasively altering the rock mass through which they travel. Moreover, once alteration has run its course, in contrast to veins, there may or may not be left any definite locus for ore deposition, and if there is, its location in relation to the alteration pattern may vary in different deposits. At least, the orebody need not be, and usually isn't confined within an envelope of the most intensely altered rocks, but may occur impressed upon any part or parts of the alteration pattern.

The foregoing several paragraphs lead up to the important conclusion, so patently demonstrated at Braden, that the main period of hydrothermal rock alteration precedes, and is distinctly separated from, the main period of metallization in porphyry-type deposits. Moreover, the structural response of a large mass of diversely-altered rocks to geologic stresses determines the localization of stockwork fracturing and consequently fixes the locus of ore deposition. These two propositions would indicate that porphyry-type deposits are a breed apart—not simply grandiose conglomerations of minute individual vein-type deposits.

Except for the narrow and relatively unimportant bleached margins along sulfide veinlets in the andesite, there is no evidence at Braden that the more pervasive rock alteration was derived from veinlets of the stockwork fracturing. The same sulfide and gangue minerals are found in veinlets that traverse all types of rocks that have undergone all degrees of alteration. In this case, the main phase of rock alteration is clearly earlier than sulfide deposition, and furthermore, there is good reason to believe that rock alteration occurred even before stockwork fracturing took place. Thus we can suggest that in the case of porphyry-type deposits, the intense, pervasive rock alteration is due to the initial porphyry intrusion. The resultant diversely-altered mass of ground is especially susceptible to stockwork fracturing, which in turn, gives access to sulfide ore deposition.

Schwartz (14), and possibly others, have flirted with the idea of sulfide deposition being impressed upon favorably-prepared portions of an already altered area. This concept would seem to provide a plausible explanation for the variable position of the orebody in relation to the alteration pattern at different porphyry-type deposits. It would also account for some of the puzzling strongly altered areas that presumably lack metallization.

Further speculation on the fundamental difference between veins and porphyry-type deposits, as suggested by the evidence at Braden, is beyond the scope of this paper. A comparative investigation of porphyry copper deposits, with this concept in mind, offers an interesting subject for further study.

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Salt Lake City 17, Utah,
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# EVIDENCE OF THE ORIGIN OF THE BLIND RIVER URANIUM DEPOSITS

DUNCAN R. DERRY

ABSTRACT

The ten uranium mines now in production in the Blind River area of Ontario have provided considerable new evidence on the origin of the deposits and have been the subject of a number of studies by Government, company, and research geologists. An attempt is here made to co-ordinate and assess the evidence and conclusions presented by the various workers.

Commercial ore is almost exclusively restricted to quartz pebble conglomerate beds near the base of the Lower Huronian quartzites and a direct relationship exists between maximum conglomerate development and grade of uranium. The detrital material was derived from Archaean basement rocks to the northwest and was probably deposited under deltaic conditions near a northward-migrating shore line.

The ore minerals are uraninite, brannerite, and minerals of the gummite group in variable proportions. Brannerite is the most generally accepted as detrital mineral but even here the evidence is not altogether convincing. Age determinations show that definite detrital minerals, such as zircon and monazite, have an age corresponding to that of the Archaean basement while the uranium minerals show an age closer to that of the deposition of the Lower Huronian sediments.

Pending more convincing evidence that the brannerite is detrital, it is concluded that:

(1) The uranium minerals were deposited contemporaneously, or shortly after, deposition of the conglomerate beds, but as precipitates from supergene solution rather than as detrital minerals.

(2) The present uranium minerals resulted from recrystallization or reaction with other minerals after burial.

(3) Hydrothermal action does not appear to have played a more significant role than aiding such recrystallization and the redistribution of uranium within the conglommerate beds.

## INTRODUCTION

THERE are now ten mines in eight separate companies[1] producing uranium from what is generally known as the Blind River area, nine being actually in the vicinity of the new Town of Elliot Lake, 20 miles northeast of the town of Blind River, and the tenth (Pronto) 18 miles east of that town. In addition one, the Spanish American mine, is on a care-and-maintenance basis, the uranium contract held by the mining company, Northspan Uranium Mines Ltd., being supplied by its two other mines. These ten mines are currently treating about 32,000 tons of ore a day of ore of a grade mainly between two and two and a half pounds of $U_3O_8$ per ton. Accordingly, there has

[1] Since this paper was written the necessity to cut back the rate of uranium production in order to extend Government contracts over a longer period has resulted in the actual and impending closing of some mines.

now been made available, since the discovery of the deposits in 1953, a considerable quantity of evidence on the geological history and processes behind their origin. Although there is far from unanimity in the conclusions of the various workers on the origin of the ores, and much room for further research, certain broad principles have been established and it seems a good time to take stock of the evidence assembled to date.

The present writer has done no original research on these problems. He has instigated and supervised some studies on mines under the management of The Rio Tinto Mining Company of Canada (these being the Quirke and Nordic mines of Algom Uranium Mines Ltd., the Panel, Lacnor, Buckles and Spanish American mines of Northspan Uranium Mines Ltd., the Milliken Uranium mine and the Pronto mine) and a good deal of the evidence presented comes from these mines. He has also had the cooperation of the staffs of the other four producing mines, as well as the benefit of earlier publications and of correspondence and discussions with Government geologists, research students and others interested in the many problems.

The paper is, therefore, a summary of evidence and a progress report rather than a detailed study of any particular phase. It is hoped that the evidence is summarized fairly, but the conclusions, naturally, cannot coincide with those of all the individual workers.

## PREVIOUS AND CURRENT WORK

Although some geological studies had been carried out in the general area of the north shore of Lake Huron before the end of the last century, the first geological mapping involving any detail, including the sub-division of the Huronian Series, was carried out by W. H. Collins (5) of the Geological Survey of Canada in 1925. This work was of high quality, as might be expected from one who later became the Director of the Survey, and the geological map produced of the Blind River area played a considerable part in the follow-up and staking of important producers in the northern part of the camp, by F. R. Joubin and his associates, after their original discovery of the Pronto deposit. Following Collins report there was no detailed work carried out in the Blind River area, so far as published reports are concerned, until after the uranium discoveries, when E. M. Abraham (1) of the Ontario Department of Mines published a preliminary map and geological notes on Townships 149 and 150. This laid the foundation for other detailed studies in the vicinity of the deposits then being developed, including those of S. M. Roscoe of the Geological Survey of Canada, who published a report in 1956 (20) dealing especially with structure contours and isopachs and their relationship to uranium values. In the meantime R. J. Traill of the Mines Department published an account of the mineralogy of the radioactive conglomerates. J. R. McDowell (11) at the same time was studying sedimentary features especially those connected with the source of material for the Huronian sediments and the direction of drainage and his very well documented report entitled "The Sedimentary Petrology of Mississagi Quartzite

in the Blind River area" was published by the Ontario Department of Mines in June, 1957.

In the meantime a number of papers had been delivered and published in various scientific journals. The first of these was by F. R. Joubin (10), the discoverer of the field, who wrote "Uranium Deposits of the Algoma (Blind River) District of Ontario" in 1954, as well as other papers including (with D. H. James) "The Algoma District" in 1956. R. C. Hart (8) and the Algom field staff summarized the developments around the Quirke Lake trough in 1955. R. T. Pountney (15) described the geology of the Algom Uranium Mine deposits in 1956. S. W. Holmes (9) published a paper on the geology of the Pronto mine in 1956, and in collaboration with geologists of the other producing or developing mines in the district wrote a brochure—prepared for the Sixth Commonwealth Mining & Metallurgical Congress—covering very well the geology of the uranium deposits and surrounding area.

The most up to date published summary of the geology of the area as a whole is that by S. M. Roscoe and H. R. Steacy (21), prepared for the Second United Nations International Conference on the Peaceful Uses of Atomic Energy. While stressing the study of the uranium-thorium ratio of the basement rocks and comparing these with corresponding ratios in the Huronian sediments, the paper summarizes very well the overall geology and the evidence to date on the origin of the uranium deposits. Roscoe (22) has also published recently a brief but valuable paper on the uranium content of the monazites.

In addition to the published papers referred to above information was obtained for the present summary from various unpublished sources and from discussions with geologists and mineralogists working in this field. These sources included correlation work being carried out under the general direction of the writer by members of the staff of mines under the control of The Rio Tinto Mining Company of Canada. A recent correlation carried out by R. C. Heim includes the results of work carried out by R. C. Hart, E. L. Evans, R. T. Pountney, J. K. B. Booth, E. J. Lees, G. Westner, M. Stuart, J. McLeod, P. Masterman. Discussions have also been held with S. W. Holmes of Consolidated Denison and with David Robertson, who has studied a number of producing mines in the district and surrounding properties and who, with N. C. Steenland, has already in the press [2] a paper on the origin of the uranium ores in which a number of new concepts are advanced.

The area has naturally attracted graduate students over the past few years and several have selected different phases of the geology and mineralogy of these deposits for their theses. Thus P. J. Pienaar, in a thesis submitted at Queen's University and to be published in part by the Geological Survey of Canada, covers the sedimentation and correlation of beds, together with an assessment of the mineralogical evidence in regard to the origin of the deposits, in a most thorough and comprehensive manner. Robert Rice also submitted a thesis at Cambridge University covering part of the same field

[2] It appeared in this JOURNAL, Vol. 55, No. 4, 1960, p. 659–694.

but stressing particularly the detrital mineral content of the sediments and its bearing on detailed stratigraphic correlation. U. G. Milne and R. G. Arnold have both made useful mineralogical studies described in theses as yet unpublished. J. Patchett is also working on a thesis shortly to be published dealing in considerable detail with the mineral content, especially radioactive minerals, of the ore-bearing horizon in the Algom-Nordic mine. D. S. Sinclair of Queen's University is working on the faults and dikes of this area and the alteration affects in their vicinity.

Age determinations are, obviously, an important aspect of the studies in regard to the origin of the uranium deposits. Determinations have been carried out in a number of laboratories including the Geological Survey of Canada, Massachusetts Institute of Technology, The Carnegie Institute, Geophysical Laboratory in Washington. The greatest number, however, have probably been carried out by the Department of Geophysics at the University of Toronto by R. M. Farquhar and others under the general direction of Professor J. T. Wilson, much of the material being separated and identified by J. Patchett.

Many of the papers referred to, either published or in preparation, deal with the various aspects of the geology of the Blind River deposits in considerably more detail than is attempted in this present paper.

## GENERAL GEOLOGY

The general geology is here dealt with very superficially and for more details the reader is referred to the bibliography and especially to the reports by the Geological Survey of Canada and the Ontario Department of Mines, and the brochure prepared for the Sixth Commonwealth Mining Congress.

Briefly the uranium deposits all occur near the base of a series of Younger Precambrian sediments, generally referred to as the Huronian, which lie with marked uniformity on the older Precambrian, or Archaean basement rocks. The Huronian sediments are gently folded to give their contact with the older basement the shape of a "Z," the upper angle of which encloses a west-pitching anticlinal core of basement.

The south-dipping south limb of the anticline, on which only the Pronto mine occurs, is interrupted by a major thrust fault, striking East and dipping South, which results in basement rocks being thrust over Huronian. Except for the Pronto mine all the uranium deposits being worked lie in two "channels" on the two sides of the syncline. The north one contains the Algom-Quirke, Consolidated Denison, Panel, Can-Met, Spanish American (inactive) and Stanrock mines. The south one contains the Buckles (main ore worked out), Algom-Nordic, Lacnor, Milliken and Stanleigh mines.

*Pre-Huronian Rocks.*—These consist of three main groups (1) Volcanics and related sediments; (2) Gneisses resulting from the granitization of sediments and possibly volcanics; (3) Massive granitic and granodioritic rocks, together with smaller basic masses. Again the reader is referred to more thorough previous studies for greater detail. The only points made here are:

(a) The basement underlying the ore deposits is more commonly predominantly the volcanics-sediments group. The river channels, in which the uranium deposits are localised, may have been influenced in place and direction by the presence of the more easily eroded basement rocks. The predominant direction of folds of these older rocks, where exposed close to their contact with the rocks of the Huronian syncline, is about 110° (True).

(b) Gneisses are rarely seen underground below the ore deposits or near the Huronian contact. They form a belt lying north of the syncline (20). Where acid intrusives are seen underlying the Huronian in underground workings they are mostly quite massive.

Roscoe has made a study of the basement rocks, particularly the granites and granodiorites, in regard to their mineral content and especially the thorium-uranium ratio. These studies show that with the exception of one or two local uraninite occurrences, there is no unusually high uranium content in the basement rocks from which the Mississagi sediments have been derived. The thorium-uranium ratio in the basement rocks varies but in general the content of $ThO_2$ is between .001% and .01% while the $U_3O_8$ is between .0003 and .003%. Thus the thorium-uranium ratio of the basement rocks lies in the general vicinity of 3:1.

*Huronian Sediments.*—This series of sediments, originally described and sub-divided by Collins (5), has been found by more recent studies to be rather more complex and a new system of nomenclature has been suggested by Roscoe. On the included table (after Robertson and Steenland (19)) the two nomenclatures are shown.

STRATIGRAPHIC SUCCESSION OF THE HURONIAN SERIES IN THE BLIND RIVER AREA (AFTER ROBERTSON AND STEENLAND)

| Nomenclature of Collins | | Nomenclature of Roscoe | | Common terminology | |
|---|---|---|---|---|---|
| Formation | Series | Group | Formation | | |
| Lorraine | Cobalt | | | Lorraine | Upper Huronian |
| Gowganda | | Dunlop | Gowganda | Gowganda | |
| Serpent | Bruce | Quirke | Serpent | Serpent quartzite | Middle Huronian |
| Espanola | | | Espanola | Espanola limestone | |
| | | | | Espanola greywacke | |
| | | | | Bruce limestone | |
| Bruce | | | Bruce | Bruce conglomerate | |
| Mississagi | | | Ten Mile | Upper Mississagi | Lower Huronian |
| | | Mississagi | Whiskey | Middle Mississagi | |
| | | Elliot | Nordic | Lower Mississagi | |
| | | | Matinenda | | |

As may be seen, the Lower Mississagi, which contains all the known commercial uranium deposits, has been sub-divided by Roscoe into the Matinenda and the overlying Nordic formation. The upper part of the Matinenda and the whole Nordic formation, however, are not seen on the north side of the syncline but are found on the south side and in the sediments sweeping southwesterly around the anticlinal nose. The overlying Whiskey formation, consisting mainly of argillites with a basal pebble and boulder conglomerate member, is the lowest member of the Huronian series that can be traced and correlated with confidence from one side of the syncline to the other. On the south side it overlies the Nordic formation but on the north side in the vicinity of Algom-Quirke and Consolidated Denison the Whiskey formation lies directly on the lower part of the Matinenda and in places overlaps it and lies directly on basement rocks.

The above relationship is consistent with the conclusion that the lower part of the Mississagi series of Collins consisted of material derived from an older land mass to the north which was deposited in deltaic conditions on a shoreline advancing in a northerly direction. This brings up the usual problem in such cases of whether to correlate formations by their relationship to the underlying rocks and the conditions in which they are formed, or by actual age. Consistent with the assumption of an advancing sea it seems most probable that the ore-bearing conglomerate and enclosing quartzite on the south side of the syncline was formed at a somewhat earlier date than were the similar ore-bearing conglomerates on the north side of the syncline. By the time the latter were being deposited it is probable that what Roscoe calls Upper Matinenda, or even the overlying Nordic sediments, were being deposited in the area now corresponding to the south limb of the syncline.

Although correlation of the Lower Huronian sediments at Pronto with the formations around the syncline is difficult, in view of the complex faulting and considerable erosion of overlying formations at Pronto, it seems likely by inference that the Pronto ore-bearing conglomerate is the oldest of all the deposits being worked. We might assume that conditions favoring the deposition of gravel beds in broad river mouths or deltas progressed from somewhere south of the location of the Pronto mine to somewhere north of the location of the Algom-Quirke mine over a period of some thousands of years.

*Intrusive Post-Huronian Rocks.*—Collins in his original study on the area definitely concluded that the Cutler Batholith, lying southeast of the Pronto deposit and on the far side of the Murray Fault, was intrusive into Huronian rocks. Although this conclusion has been accepted by many later workers, I can find no one who has described in print, or is prepared to show physically, any place where there is positive proof of granitic rocks intruding Huronian sediments. It is not argued here that such do not exist, but that field proof is still necessary before Post-Hurionian granites in this area can be positively accepted. Isotope age determinations (21), while not entirely satisfactory, support a post-Huronian age for this granite.

As mentioned later, albitization and related alteration is prevalent in several of the mines, particularly in Pronto. This may be taken as an

implication of intrusive activity but since this type of alteration is restricted to the vicinity of faults or fracture zones all that can be concluded with confidence is that hydrothermal solutions, particularly of a sodic character, were prevalent at the time Huronian rocks, south of the present line of the Murray Fault, were being disturbed or involved in mountain building movements.

Dikes and sills of diabase are common, intruding the Huronian sediments, and appear to be of more than one lithological type of rock; some of the later dikes may possibly be classed as lamprophyres. Alteration of several types has been described in the vicinity of certain of these dikes. While one type consisting largely of chloritization does seem directly related to diabase intrusion this is of rather local extent. The red albitization of quartzite does occur in the vicinity of certain dikes particularly on Algom-Nordic, Panel and Can-Met. It seems probable, however, that the relationship with diabase is fortuitous and may result from a fault along one wall of the diabase permitting the access of albitizing solutions. Certainly red albitization is not a constant feature of the sedimentary rocks in contact with diabase.

## THE ORE-BEARING CONGLOMERATES

There is a close similarity between all ore-bearing conglomerates from the Pronto mine in the south to the Algom-Quirke mine in the north. In all cases the conglomerates consist largely of quartz pebbles with some pebbles of black chert, and rarely "foreign" pebbles, embedded in a darker matrix. The matrix consists of fine-grained quartz, feldspar, and sericite and has a variable but considerable content of pyrite, generally between 15 and 25 percent of the matrix in ore-grade conglomerate. It carries such heavy minerals as zircon and monazite, and the uranium minerals are invariably restricted to this matrix. The thickness of uraniferous conglomerate beds varies up to 12 feet or so but in certain cases—mainly by the merging of several conglomerate bands—a thickness of 20 to 30 feet may be reached.

The relationship of the ore-bearing conglomerate to the basement varies from the Pronto mine, where it is almost everywhere a basal conglomerate, to the sitation on both sides of the syncline where the ore-bearing conglomerate may lie 100 feet or so above the basement but may approach or touch it locally where the original basement floor formed topographic "highs."

The number of conglomerate beds containing a sufficient proportion of uranium to be considered as millfeed varies from the single basal conglomerate at Pronto to the four or five distinct horizons on the north side of the syncline. Many other conglomerate beds, generally narrower or less consistently developed, carry sub-commercial proportions of uranium.

*Correlation of Conglomerates.*—As explained earlier it is believed that similar conditions favoring the deposition of conglomerates advanced from south to north over a fairly extended period. Accordingly, it would not be expected that direct correlation could be established between the individual conglomerate bands at Pronto and the "South Limb channel" on the one hand, or between the latter and the "North Limb channel" on the other.

Within each of the last two channels, however, correlation can be established to some extent as shown below.

### THE ORE CHANNELS

The deposits being worked are restricted to three separate "channels" believed to be river beds reaching deltaic conditions. One, on which the Pronto mine is situated, is curtailed down-dip by thrust faulting. The other two, on each side of the Elliot Lake syncline, are well marked and give every appearance of drainage channels. In addition to the three, described below, some other less-marked "channels" have been indicated by drilling and show some development of quartz conglomerates with minor radioactivity but not, so far, of mineable grade.

*The Pronto Zone.*—The deposit that became the Pronto Uranium Mine was the first discovery of commercial grade uranium in the district. It is also the shortest zone or channel carrying uranium due to the fact that its continuity is interrupted a few hundred feet down dip from the surface outcrop by a zone of thrust faulting bringing older basement rocks upwards and over the Huronian sediments containing the ore (Fig. 1).

Pronto differs from the other producing mines in that the ore-bearing conglomerate is right at the base of the Huronian Series lying either directly on basement rocks or on the saprolites or fossil residual soils. The conglomerate is up to 10 feet thick consisting of predominantly quartz pebbles. The detailed geology is more complex than that of the other mines due to much faulting and fracturing and the intense localized alteration associated with this fracturing.

The western limit of the ore channel trends in a northwest-southeast direction. This western limit is formed near surface by a scoured channel but the same southeasterly trend appears to persist in the lower levels beyond the influence of the scour channel, the limit here being caused by thinning of the basal conglomerate against the gradually rising basement. The eastern limit of the conglomerate bed trends in a north-south direction, almost directly down dip, for the first few hundred feet from surface and then appears to swing southeasterly. This eastern limit occurs by the thinning of the conglomerate and interfingering with quartzite. Thus the zone gives the appearance of a shallow channel in which a gravel bed was deposited as the basal member of a predominantly sandy series of much greater lateral extent.

The locally intense hydrothermal alteration, now receiving detailed study by the Pronto geological staff, is too complex a problem to be adequately dealt with here. It may be briefly observed, however, that (1) The alteration, in which albitization plays a major part but which also includes carbonate replacement, has the effect of changing the yellowish quartzite into a salmon pink mass resembling a syenite intrusive. The ore-bearing conglomerate is also affected, first the matrix being replaced and in the more advanced stages even the quartz pebbles being completely obliterated. (2) Surprisingly enough the uranium values have not been removed, but remain in the original stratigraphic position although in places compressed into a smaller thickness

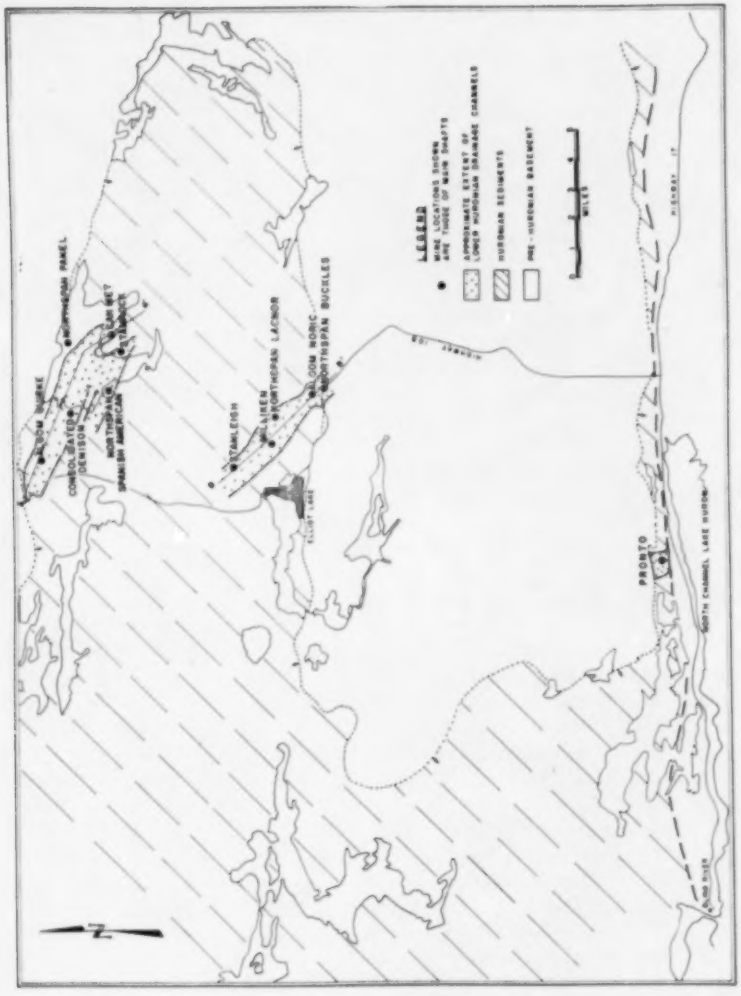
LEGEND
MINE LOCATIONS SHOWN
ARE THOSE OF MAIN SHAFTS
APPROXIMATE EXTENT OF
LOWER HURONIAN DRAINAGE CHANNELS
HURONIAN SEDIMENTS
PRE-HURONIAN BASEMENT
MILES
N
BLIND RIVER
COBALT-GAVER
GEMISON
NORTHPORAS
SPANISH MATTAGAMI
ELLIOT LAKE
STANLEIGH
ALGOMA
NORTHPORAS
BLOOM NORIC
NORTHSPAN BUCKLES
PRONTO
SOUTH CHANNEL LAKE HURON

FIG. 1.

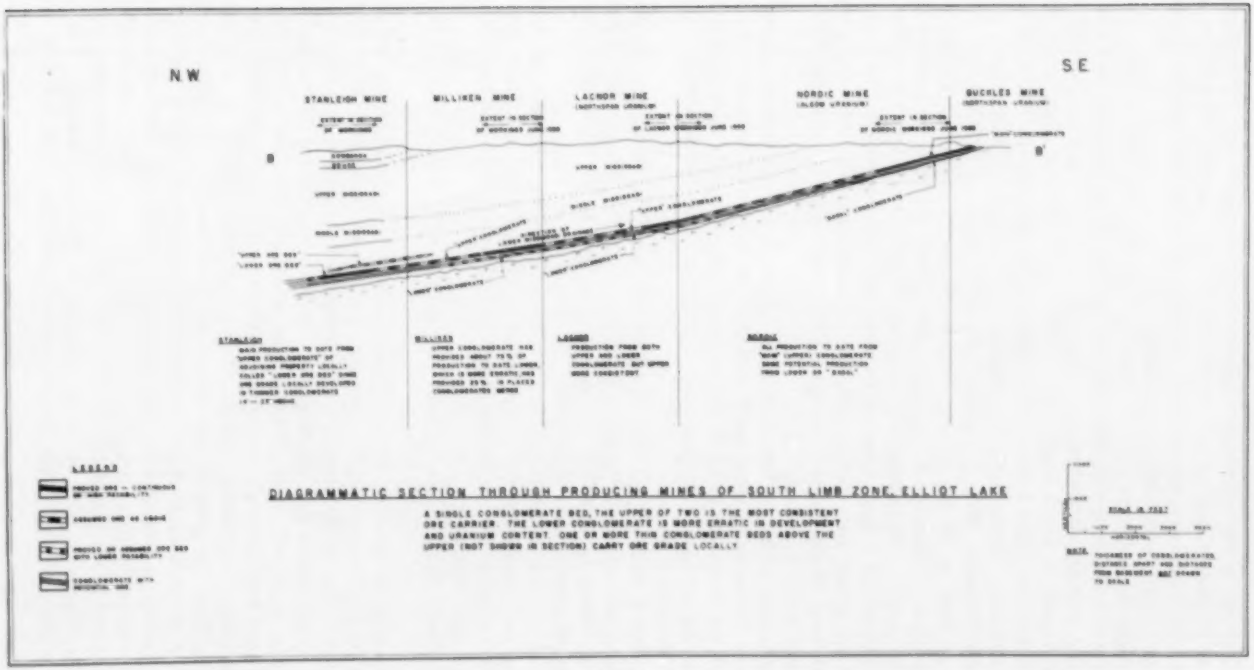
NW
SE
STANLEIGH MINE
MILLIKEN MINE
LACNOR MINE
NORDIC MINE
BUCKLES MINE
B
B'
DIAGRAMMATIC SECTION THROUGH PRODUCING MINES OF SOUTH LIMB ZONE, ELLIOT LAKE
A SINGLE CONGLOMERATE BED, THE UPPER OF TWO IS THE MOST CONSISTENT ORE CARRIER. THE LOWER CONGLOMERATE IS MORE ERRATIC IN DEVELOPMENT AND URANIUM CONTENT. ONE OR MORE THIN CONGLOMERATE BEDS ABOVE THE UPPER (NOT SHOWN IN SECTION) CARRY ORE GRADE LOCALLY.

FIG. 2

than maintains in the adjoining unaltered conglomerate. (3) The alteration is clearly related to faulting and fracturing, certain "panels," defined by near-vertical fractures, being altered while the adjoining "panels" are left relatively unchanged from their normal appearance.

It might be expected that the uranium-bearing minerals in such altered areas would have been recrystallized and perhaps reconstructed and it is not surprising that age determinations from this mine have shown anomalies.

*The Nordic or South Limb Zone.*—The Nordic zone or channel lies on the south limb of the Elliot Lake syncline and extends in a northwesterly direction with increasing depth from the Buckles and Algom-Nordic mines to the Stanleigh Uranium Mine, for a total proved distance of 19,000 feet. As far as can be seen, at all five mines (Buckles, Algom-Nordic, the Lacnor Mine of Northspan, Milliken and Stanleigh) the same conglomerate horizon is the main ore carrier. A second conglomerate 10 feet or 15 feet below the first (and constituting a basal member in some parts of the Algom-Nordic mine) carries ore grade and width much less constantly in all four mines, and a third horizon above the main conglomerate may also be found to reach ore grade and width in places.

The lateral width of the channel in which the conglomerate appears to have been deposited is from 4,400 to 6,000 feet measured normal to the axis, although the limits are in many places based only on widely spaced drill holes between the areas of underground workings. The lateral limits may be formed in several ways:

(1) By a thinning of the conglomerate and fingering out to give a decreasing ratio of conglomerate to quartzite. This is probably the commonest way that mining is limited in the lateral sense and is the factor causing most of the northeastern limit of the ore.

(2) By a rise in the basement rock resulting in the conglomerate horizon thinning and eventually being wedged out. This occurs in certain parts of the western age of the ore in the Algom-Nordic mine and in certain places in Milliken and Stanleigh.

The lateral limit of ore by later "scouring" is not a factor in the Nordic Zone.

Although the present trend of this channel is angling across the north dipping limb of a syncline, the evidence of sedimentation (11) shows that the original direction of the drainage that transported the gravel and sand making up the conglomerate and quartzite was from the northwest to the southeast.

*Quirke or North Limb Zone.*—This is the most northerly ore zone of those found and although occurring in almost exactly similar rock types as the previously mentioned deposits, it was probably formed at a somewhat later date than the others, consistent with a northward migrating shoreline. The zone or channel runs from northwest to southeast and is traced from Algom-Quirke, where it outcrops, through Consolidated Denison and over the boundaries of that property into Panel and Can-Met. As mentioned below the ore in the Spanish American and Stanrock properties may be on a tributary channel or may be on the margin of the main channel. The total length in the direction of the channel in which ore has been found is 32,000

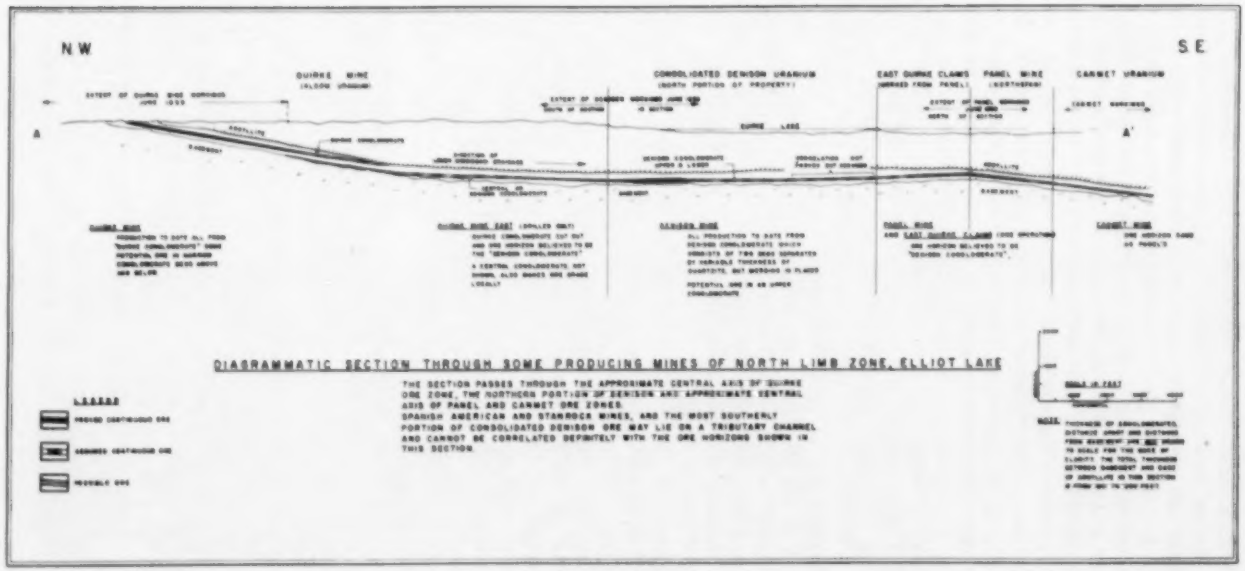
NW
SE
A
A'
QUIRKE MINE
CONSOLIDATED DENISON URANIUM
(NORTH PORTION OF PROPERTY)
EAST QUIRKE CLAIMS PANEL MINE
CANNET URANIUM
QUIRKE LAKE
DIAGRAMMATIC SECTION THROUGH SOME PRODUCING MINES OF NORTH LIMB ZONE, ELLIOT LAKE
THE SECTION PASSES THROUGH THE APPROXIMATE CENTRAL AXIS OF QUIRKE ORE ZONE, THE NORTHERN PORTION OF DENISON AND APPROXIMATE CENTRAL AXIS OF PANEL AND CANNET ORE ZONES. SPANISH AMERICAN AND STANROCK MINES, AND THE MOST SOUTHERLY PORTION OF CONSOLIDATED DENISON ORE MAY LIE ON A TRIBUTARY CHANNEL AND CANNOT BE CORRELATED DEFINITELY WITH THE ORE HORIZONS SHOWN IN THIS SECTION.

FIG. 3

feet and the width varies from 6,000 to 9,600 feet, measured at right angles to the direction of flow of the channel. Correlation of ore-bearing conglomerates from one property to another is much more difficult than in the South Limb zone due to the greater number of conglomerates and to the rather large gaps in which there are no mine workings or drill information. Recent studies by E. J. Lees and R. C. Heim in connection with an attempt at correlation by the Rio Tinto staff, with collaboration from the geological staffs of the mines concerned, suggest that the conglomerate of the main ore horizon in the Quirke mine (the "Quirke Conglomerate") dies out or deteriorates (in places wedging out against an overlying erosion surface) as it reaches the east and southeast part of that property, its place as the main ore-grade carrier being taken by a conglomerate 60 to 100 feet lower down in the series. This lower conglomerate, which has been variously referred to as the "C" zone and the "Denison Conglomerate" is the one that carries the most consistent ore in Consolidated Denison. This consists of two conglomerate beds separated by up to 15 feet of quartzite, but in places the latter thins to a point where both conglomerates can be profitably mined as one body.

Correlation of the Denison conglomerate with the main ore conglomerate in the Panel mine (and in some claims owned by Algom Uranium between the two) is now accepted with fair confidence. Similarly it is probable that the horizon forming the ore conglomerate in the Can-Met mine can be correlated with that in Panel.

The conglomerate carrying the ore in the Spanish American mine and that in the Stanrock mine are almost certainly the same. On the other hand it is doubtful if the ore horizon in these two can be correlated with that being mined in Denison and Panel because the two areas are separated by a basement ridge that cuts out the lower, ore-bearing portion of the series. Rice (18) considers the Spanish American-Stanrock zone a separate channel, a tributary that joins the main channel further east, basing his conclusion on a difference in the proportions of the detrital minerals. D. S. Robertson, on the basis of measurement from the overlying "Whiskey Conglomerate," believes the Spanish American-Stanrock ore conglomerate to be lower in the series than the Denison conglomerate.

From the above it may be concluded that two and probably three separate conglomerate beds play the part of the main ore horizon in different parts of the channel, i.e. the main ore "steps down" from one conglomerate to an overlapping lower one.

At any one mine, in addition to the "main" ore conglomerate, narrower conglomerate layers carry smaller proportions of uranium that may make ore grade over sufficient thickness to be mined in selected areas. Thus at the Quirke mine in addition to the main Quirke Conglomerate there is an "Upper Conglomerate" 8 feet above and a "Lower Conglomerate" 13 feet below, both of which may later be mined in selected areas.

The lateral limits of the ore-bearing conglomerates in the Quirke channel are formed in several ways:

(1) By the conglomerate being cut out from above by an old erosion surface formed prior to the deposition of the overlying Whiskey formation.

At the west end of the Quirke mine erosion takes the form of a scoured channel. The northeast limit of ore in Quirke mine, as well as in the Panel mine, is formed by a more regular erosion surface, again overlain by Whiskey formation.

(2) By gradual thinning of the conglomerate and fingering into quartzite.

(3) By the conglomerate wedging out against a basement ridge. This is a local rather than regional effect. One example is in the west part of the Denison mine south of the Quirke boundary, another the basement ridge dividing the Panel-Can-Met ore from the Stanrock ore.

### MINERALOGY OF THE ORE-BEARING CONGLOMERATE

No attempt is made here to discuss in detail the mineralogy of the ore-bearing horizons, which has been dealt with in papers by Roscoe, Traill, and Ramdohr as well as by Pienaar, Milne, Arnold, Rice, and Patchett in work as yet unpublished. The main conclusions that the present writer derives from these studies, so far as evidence of origin is concerned, are as follows:

The minerals of significance, either as carriers of uranium and thorium or from the standpoint of evidence of the origins of these metals, are: uraninite, brannerite, gummite, thucolite, monazite, zircon, and pyrite.

*Uraninite* is relatively less abundant than brannerite in the north limb ore channel and is most abundant in the Algom-Nordic mine on the south limb channel. Most of those who have studied it under the microscope describe it as "angular to sub-rounded." The typical grains do not appear to be as rounded as one would expect of detritals, although Ramdohr and D. S. Robertson have described rounded grains. However, the uraninite carries about 6% $ThO_2$, which is more typical of pegmatitic uraninite than vein types, thus tending to favor a detrital origin. The two age determinations (see below) that seem most reliable give an age of about 1,700 m.y., which would, if accepted, make a direct detrital origin impossible.

Holmes, Pienaar, Roscoe, Arnold, and Robertson all seem to accept the uraninite as detrital. Rice believes it to be formed by "secondary precipitation" of uranium leached out of brannerite, deposited as gummite and recrystallized as uraninite as a result of energy provided by the heat of intruding diabase. Patchett also regards uraninite as of secondary origin. Patchett's observation that some uraninite grains show, under the microscope, carbon centres is of great significance if it can be proved that this feature is widespread in the district.

Davidson in the references quoted and in many contributions to "Discussions" in Economic Geology has produced an impressive arsenal of evidence and argument against a detrital origin of uraninite, which must be given careful consideration whether or not one is ready to follow him to his final conclusions on the origin of the mineral in the Blind River and Witwatersrand deposits.

*Brannerite.*—There has been much discussion about this mineral and opinions vary from those who regard it as the most important detrital uranium-carrying mineral to those who consider that brannerite, as a natural

mineral, does not really occur at all in the Blind River ores. All agree that the grains, which generally have a rounded appearance, are now largely metamict, containing blades of anatase and rutile. The mineral carries a variable proportion of uranium, generally rather lower than typical brannerite from other parts of the world.

Rice notes a variation in the degree of "alteration" from relatively pure grains to those in which only an aggregate of rutile and anatase remain. The alteration appears to start with the appearance of drusy cavities and is followed by ex-solution of rutile in planes within the grain. He notes that while the amount of alteration may vary in adjacent grains the *average* alteration increases "down stream." He thus believes the original detrital grains were relatively pure and massive brannerite and have been progressively altered to the extreme stage of an aggregate of rutile and anatase with little remaining uranium.

Pienaar (16) describes (under the term "Two phase uranium-titanium compound") the same phenomenon and concludes that the mineral was deposited in detrital grains but in an unstable form due to leaching of uranium during transportation. He further suggests "subsequent recrystallization probably resulted in the diffusion or ejection of the uranium from the bladed aggregates."

Robertson and Steenland (19) believe that the brannerite grains are detrital in their present shape and metamict character but have undergone some subsequent alteration.

Patchett (14) concludes that metamict brannerite grains from the Algom-Nordic mine are residual and occurred in this form in their original source rocks although he suggests the rutile needles included in the grains may be the result of alteration. He attempted to synthesize brannerite and was only able to do so at 2000° C in an inert atmosphere and concludes it could not have been formed naturally in the way suggested by Ramdohr (below).

Ramdohr (17), on studying brannerite from the Pronto mine, describes the mineral in the form of reddish-brown splinters forming part of larger metamict grains. He concludes that the brannerite is *not* a detrital mineral but one generated in situ as pseudomorphs of both rutile and uraninite by what he terms the "Pronto Reaction" which he suggests occurs according to the formula:

$$UO_2 + 2 \text{ to } 3\ TiO_2 \rightarrow UTiO_{2-3}O_{6-8}.$$

Most of those who have studied the mineralogy of these ores agree that a mineral of the present delicate and metmict character is unlikely to be transported as a resistant detrital. On the other hand the shapes of the grains are typically detrital. It thus becomes a question of whether the grains were originally purer and more massive brannerite that have become subsequently altered or whether the grains were originally some other, probably titaniferous, mineral into which uranium has been introduced.

*Gummite.*—Under this term is included a number of so-called secondary or alteration products containing uranium, appearing to the naked eye as small yellow grains. The mineral is particularly noticeable in the higher grade

ores in the Pronto mine, but may also be found in the high-grade material on both sides of the Elliott Lake syncline. Rice (18) notes that at the Spanish American mine (over 3,000 feet depth) gummite is the second commonest uranium mineral after brannerite. He also notes that gummite is relatively scarce where uraninite is common.

*Thucolite.*—This mineral, which is found exclusively on late fractures or slip planes within the ore-bearing conglomerate, is radioactive and carries a variable proportion of uranium, evidently derived from the "primary" uranium minerals in the radioactive conglomerate and reprecipitated on fractures still within the same bed. Quite commonly it has pyrrhotite associated with it.

*Monazite.*—The monazite in the conglomerates gives every appearance of being a detrital mineral, appearing in well-rounded grains. Roscoe has noted in a recent paper that the monazite from the Blind River ore conglomerates carries an unusually high proportion of uranium, the average being about 1.5% $U_3O_8$ and 6% $ThO_2$. He also notes that a part of the uranium and thorium is dissolved during the acid leaching treatment of the ores so monazite must be regarded as one of the uranium-bearing ore minerals.

The monazite grains carrying the highest uranium content are gray and have indefinite patches of what may be uranothorite. Thus there appears to be some question as to whether the high content of uranium is original or whether it has been added by replacement after the original monazite was deposited as a detrital grain.

The monazite separated by Patchett and dated by J. A. Mair (of the Department of Geophysics at the University of Toronto) at 2,550 m.y. was the normal yellow type. Both Patchett and Milne doubt whether the gray, highly uraniferous "monazite" should come under that name, i.e. they think it may be an alteration product. Milne refers to it as a "monazite complex."

*Zircon.*—This mineral is, without doubt, a detrital one in the Blind River ores. The zircon is commonly of the purple radioactive type. Dating by J. A. Mair on grains from the Quirke mine gave an age of 2,450 m.y.

*Pyrite.*—Pyrite is a common constituent of the matrix of the ore conglomerates forming about 15 to 25 percent of the matrix in well packed conglomerates. There are two types of pyrite. One, the later, is relatively coarse, forms irregular replacements in the older type. The other, and older, type is fine grained and granular and in places gives the appearance of bedding. R. G. Arnold (3) notes that many of these pyrite grains have leucoxene centres and suggests that the pyrite resulted from the sulphurization of titaniferous magnetite. This seems a logical conclusion in the absence of magnetite in a bed resulting from a well sorted gravel where magnetite and ilmenite would be expected to be common constituents.

Roscoe agrees with the titaniferous magnetite origin of the granular pyrite. Robertson and Steenland, however, believe the granular pyrite was deposited as detrital, as does Rice, and Pienaar, although not specific on this point, implies the same belief.

The somewhat conflicting evidence on the minerals dealt with may be summarized as follows:

(1) Zircon, and at least the "normal" yellowish monazites, accepted as detrital minerals.
(2) Gray, high-uranium monazite presumably detrital but possibly altered by uranothorite replacement after deposition.
(3) Gummite—all agree not detrital. Difference of opinion as to whether it is secondary after uraninite and brannerite, or formed directly or indirectly by chemical precipitation from supergene solutions.
(4) Uraninite—by some regarded as detrital, by others as a secondary precipitation.
(5) Brannerite—considerable difference of opinion.
(6) Pyrite—Two schools of thought in regard to the older pyrite: (a) By sulphurization of titaniferous magnetite, (b) By deposition of detrital pyrite. Agreement that younger pyrite is hydrothermal.

## AGE DETERMINATIONS

Age determinations on sediments such as the uraniferous conglomerates are of little value unless carried out on cleanly separated, and identified, mineral grains.

Stieff and Stern (23) were among the first to report determinations on several specimens by several methods. The results, however, were ambiguous due possibly to incomplete mineral separation but also because many of the determinations were on material from the Pronto mine where alteration of a type and degree not typical of the areas as a whole is prevalent.

More recently at the University of Toronto, the Department of Geophysics, using the Pb 206/207 method on material carefully separated by J. D. Patchett of the Department of Geological Sciences, has obtained results that seem technically acceptable. These results, recently published under the authorship of J. A. Muir, A. D. Mayne, J. D. Patchett and R. D. Russell (25), are as follows:

| Mineral | Source | Laboratory & worker | Method | Calculated age in m.y. |
|---|---|---|---|---|
| 1. Monazite | Nordic Mine Separated by J. D. Patchett | Department of Geophysics U. of Toronto J. A. Mair | PB206/207 | 2,550 |
| 2. Zircon | Quirke Mine Patchett & Roscoe | Department of Geophysics U. of Toronto J. A. Mair | PB206/207 | 2,450 |
| 3. Uraninite | Nordic Mine Patchett | Department of Geophysics U. of Toronto J. A. Mair | PB206/207 | 1,680 |
| 4. Uraninite | Nordic Mine Patchett | Department of Geophysics U. of Toronto J. A. Mair | PB206/207 | 1,740 |
| 5. Brannerite | Nordic Mine Patchett | Mair, Slawson & Chinnery | PB206/207 | 1,870 |
| 6. Brannerite | Nordic Mine Patchett | Mair, Slawson & Chinnery | PB206/207 | 2,000 |

While far more determinations are required before they can be accepted with complete confidence, these results are significant in that (i) the minerals

of undoubted detrital origin (zircon and monazite) gave an age corresponding to the average age obtained from samples of the Keewatin province that forms the basement source; (ii) the uraninites gave an age that corresponds with that believed, from geological evidence, to correspond with early Huronian sedimentation. The brannerite ages, although checking each other, are somewhat ambiguous but if, as the studies suggest, there has been some removal of uranium since their formation, the necessary adjustment would throw the dating a maximum of about 200 m.y. in the direction of that of the uraninite, i.e. to about 1,800 m.y. Ramdohr, consistent with his belief that the brannerite is formed in place by "Pronto Reaction" regards radioactive dating on this mineral as meaningless.

## CONCLUSIONS

Out of the clamor of differing opinions on the origin of Blind River uranium ores certain aspects stand out on which there is substantial agreement. These are:

(1) The source of the clastic material making up the Lower Mississagi formation was from the Archaean basement rocks to the northwest. It is also agreed that the detrital minerals at least include the zircon and "normal" monazite.

(2) The conglomerates and associated quartzite were deposited as gravel and sand in broad, river valleys or deltas near a shoreline that was advancing in a northerly direction—resulting in the overlapping by younger beds over older.

(3) Commercial grade ore is confined to certain quartz pebble conglomerate beds within 150 feet of the base of the formation. It favors the better developed and more consistent conglomerates and the best grade and width of ore in any one horizon normally coincides with that part of the bed where the thickness of conglomerate and degree of pebble packing are at their maxima.

(4) Hydrothermal alteration has affected the Mississagi sediments and, in places, the ore horizons but there is no evidence that such solutions have introduced uranium from outside or removed any measurable amount from a uranium-bearing horizon.

Opinions on the origin of the ores vary from a hydrothermal process, or some modification of it, to a "pure" detrital origin. No geologist I know in the area, however, accepts an extraneous hydrothermal origin and since the arguments refuting such origin have been well summarized by Roscoe and Steacy (21), no time will be taken here to repeat them. Most, if not all, those geologists who have studied the area believe that the uranium and thorium were deposited at about the same time as the conglomerates were laid down and were buried with them. The differences are centred mainly on the form in which the uranium was originally deposited and whether as a detrital mineral or as a precipitate from supergene solutions, and on the extent of later alteration or redistribution.

Any theories or conclusions must take into consideration the following points in the mineralogical evidence:

(a) The relative rarity of uraninite in some mines especially in the ores on the north side of the syncline.
(b) The rounded outlines but delicate, metamict character of the brannerite grains and the variation in composition and texture along the axis of a channel.
(c) The gray monazite grains that Roscoe has shown carry an unusually high uranium content, apparently in patches of uranothorite.
(d) The presence of gummite or related minerals in places and at depths where it could not be a secondary alteration related to present surface.
(e) The age determinations indicating "normal" monazite and zircon as having an age of about 2,500 m.y., equivalent to that of the Archaean basement, while uraninite and brannerite give younger ages in general grouping around 1,700 to 2,000 m.y. (Some much younger ages have been obtained and may represent later recrystallization—but have not been confirmed.)

If we eliminate a purely hydrothermal (epigenetic) origin, as supported by Davidson (7), the explanation of the origin of uranium advanced in the various papers published or in preparation may be roughly summarized under three groups:

(1) That both uraninite and brannerite are detrital minerals, account originally for all the uranium present, and have undergone some alteration at some stage following deposition. Gummite would be one result of such alteration.

(2) That uraninite is the only original uranium mineral (excluding monazite from this definition) now recognizable and all other uranium minerals, including brannerite, have been formed in situ from uranium derived from the uraninite.

(3) That brannerite is the main or sole uranium-bearing mineral (if we exclude monazite) and that uraninite is a secondary precipitation resulting from the breakdown of brannerite, aided by hydrothermal action.

For my own part, if I had to accept one of the above three hypotheses on the basis of the evidence I would pick the last. There are, however, certain pieces of evidence, or lack of evidence, that make it difficult for me to accept even this explanation: These are:

(a) Brannerite has not yet been identified in the Archaean source rocks to the northwest.
(b) Could a mineral (brannerite) be resistant enough to form detrital grains, yet be subject to alteration to a delicate metamict aggregate during or shortly after transportation?
(c) Age determinations do not support a detrital origin for uraninite or brannerite.

(d) A detrital origin postulates a completely different process from that which formed the other major type of sedimentary uranium deposit, that found in the southwestern United States. Geological principles and processes have a habit of repeating themselves, even over the changing physical conditions of a billion and a half years.

It is suggested that the rivers depositing the quartz-pebble conglomerates drained an area containing small proportions of uranium but that little reached the conglomerate beds in the form of detrital grains. Uranium and thorium, dissolved in the surface waters, would be precipitated in concentrated quantities only under specially favorable conditions that would include high porosity, slow drainage and reducing conditions.

In line with the above notion Brotzen (4) has suggested that the conglomerates might have received their uranium after light burial under sand or clay by the agency of underground water courses, such as are common in many desert areas. This would give the slow seepage and, possibly, reducing environment favorable for such precipitation.

It is suggested here that the above conditions resulted in the deposition of uranium, and some thorium in addition to what was already present as monazite etc., in the form of relatively unstable minerals. The gummite present, if not an original mineral, is probably closer to such original precipitates than any others now formed. The same conditions could also have favored the sulfurization of magnetite thus producing the granular pyrite in the ground mass.

The next stage, which might have commenced any time after the conglomerate had been buried under a few thousand feet of sediments, would be the re-dissolving of uranium and its re-deposition as uraninite or as replacement by uranothorite in parts of monazite grains, or as needles or slivers of brannerite by reaction with titaniferous minerals, as suggested by Ramdohr (17).

While hydrothermal solutions, in the sense of solutions associated with igneous intrusion, may have played part in this latter conversion, certain evidence suggests this was not paramount:

(a) The age determinations of uraninite by the Department of Geophysics at the University of Toronto gives ages corresponding to early Huronian time, before the later igneous action.

(b) Brannerite is just as common on the north side of the Elliot syncline—farthest from known later-Huronian igneous and tectonic activity—as at Pronto which is closest to this disturbance.

Doubtless the solutions responsible for albitization of quartzite and conglomerate at Pronto, and less markedly so further north, did result in some later solution and redeposition of uranium. The evidence suggests, however, that most of the uranium-bearing minerals, and the granular pyrite, were in their present form before any flood of hydrothermal solutions caused albitization, chloritization and the deposition of the later pyrite. It is particularly noticeable at the Pronto mine that the intense alteration, in places completely destroying even the quartz pebbles as well as replacing the ground mass and

the quartzite lying above the ore conglomerate, has not resulted in the uranium values being moved out of the zone.

Thus the mode of origin favored in this paper, on the basis of the evidence to date, is that the uranium was deposited more or less contemporaneously with the quartz pebble conglomerates, but not predominantly as detrital grains, and was later largely redeposited by recrystallization as uraninite or by reaction with detrital grains. The hydrothermal action associated with the tectonics and intrusions at the end of Huronian time probably caused some recrystallization or reconstitution but without moving the uranium from the original sedimentary horizons.

An open mind must be kept on this problem and it is possible that further evidence will build up an irrefutable case for a predominantly detrital origin of the uranium in the Blind River deposits. At the moment the evidence seems to the writer to be insufficient to support a process that has not apparently been repeated since Precambrian times.

Rio Tinto Mining Co. of Canada,
Toronto Canada,
*February 2, 1960*

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# OXIDATION OF SULFIDE ORE BODIES, 1. GEOCHEMICAL ENVIRONMENTS IN TERMS OF Eh AND pH

MOTOAKI SATO

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ABSTRACT

The probable ranges of oxidation potential and pH values for the weathering environment and those for the depth environment were studied through three approaches, namely field measurements of Eh and pH values of natural waters in mining districts, experimental oxidation of

iron and manganese solutions by air, and theoretical considerations of chemical and mineralogical factors involved in natural systems. The oxidation potential for the weathering environment is found to be largely controlled by the reduction mechanism of oxygen. Hydrogen peroxide forms during the reduction of oxygen in aqueous solution, and is catalytically decomposed back to oxygen plus water by various elements, some of which are common in natural systems. A reversible equilibrium is thus established between hydrogen peroxide and oxygen, resulting in the control of the oxidation potential of the weathering environment by the $H_2O_2$-$O_2$ couple. The oxidation potential for the depth environment is probably controlled by oxidation-reduction reactions involving iron-rich minerals, since iron is the most common among the elements that occur in more than one state of oxidation in rocks. Limitations may be imposed on the pH values for these environments by the dissociation of ferric hydroxide at the acidic side, and by the hydrolysis equilibrium of calcite at the basic side. An Eh-pH diagram indicating the probable ranges of Eh and pH values for the two environments is given.

## INTRODUCTION

*Geochemical Environments in Terms of Eh and pH.*—When exposed to the weathering processes, a sulfide ore body tends to develop a zonal arrangement of different mineral associations which reflect various degrees of oxidation. Minerals tend to reach equilibrium with their environments, and the change in one or more of the environmental factors results in a change in mineral association. If a mineral can no longer exist in the new environment, it undergoes chemical reactions and the reaction products may either be removed from the system or form a new mineral that is stable under the new conditions. Each mineral has a characteristic range of chemical immunity. Accordingly, a certain amount of environmental change may affect one mineral but not another; a change in the mineral assemblage results.

It is a very useful method to express geochemical environments quantitatively in terms of oxidation potential (often referred as Eh or redox potential) and pH, although these two quantities are the consequence of an over-all chemical balance of the entire substances present, and not vice versa. If Eh and pH values of a wet system are given, it is possible to predict the activity ratios among various chemical species of an element with the aid of thermodynamic calculations. An assumption is involved in this method of describing a geochemical environment, namely that the Eh and pH values of a geochemical system are largely controlled by the chemical properties and relative amounts of predominant reactive substances present, and can be treated as fixed quantities so long as those substances remain dominant or constantly supplied to the system. Other substances present in minor amounts are expected to stay conformable with the fixed Eh and pH.

*Previous Work.*—Theoretical applications of oxidation potentials to geochemical problems were discussed by Butler and Burbank (10), Goldschmidt (22), Scerbina (47), and Chapman and Schweitzer (11). In recent years, the role of pH has been incorporated into discussions of the role of oxidation potential. Such contributions were made by Mason (41), Blumer (5), Krumbein and Garrels (36), Garrels (19, 20, and 21), Huber and Garrels

(27), Baas Becking and Kaplan (2), and Huber (28). A paper that particularly refers to the problem of oxidation and supergene enrichment is one by Garrels (20).

Results of actual measurements of Eh, with or without accompanying pH measurements, are fairly common for soils, lake waters, lake sediments, sea waters, and marine sediments. Measurements for other environments are scarce. Measurements on soils were reported by Willis (61), Burrows and Gordon (9), and Pearsall and Mortimer (43). Those on lake sediments, lake waters, or bog sediments were made by Kusnetzow (37), Hutchinson, Deevey, and Wollack (30), Allgeier, Hafford, and Juday (1), Firtion (18), Swain and Prokopovich (55, 56), and Swain (57). Data for sea waters or marine sediments were given by Brujewicz (8), ZoBell (68, 64), Cooper (13), and Breurich (6). Measurements on sampled vanadium ores were made by Pommer (44). Kaplan (33) measured the Eh and pH values of 27 samples from hot springs, geysers, and pools of the geothermal regions of New Zealand. No measurements appear to have been made on sulfide ore bodies.

*Scope of Present Investigation.*—In order to provide necessary field data for the study of geochemical environments of exposed sulfide ore bodies, field measurements *in situ* of Eh and pH values of natural waters surrounding ore bodies have been carried out at various depths in mining districts. The following four mining districts were chosen: (1) Magma mine, Superior, Ariz.; (2) San Manuel mine, San Manuel, Ariz.; (3) Cole and Campbell mines, Bisbee, Ariz.; and (4) Continental No. 1 mine, San Juan County, Utah. An experimental study on the oxidation of iron and manganese solutions by air has been made to obtain additional information for the interpretation of the field data. An attempt was made to specify the probable ranges of Eh and pH values for the weathering environment where free oxygen is abundant, and those for the depth environment where sulfide minerals remain unoxidized, on the basis of these results as well as theoretical considerations of chemical and mineralogical factors involved in natural systems.

## FIELD MEASUREMENTS OF Eh AND pH

### *Method of Investigation*

*Procedure.*—The field equipment for the measurements of Eh and pH values of natural waters in mining districts consists of a probe containing three electrodes and a portable potentiometer. The structure of the electrode probe is shown in Figure 1. A plastic tube, 1¼ inches in diameter and ¼ inch thick, was cut to a length of 4 inches. Numbers of ¼ inch holes were drilled into the lower two-thirds of the tube to provide inlets for seeping water. A round plastic disc with the same diameter and similar holes was cemented to the lower end of the tube to complete the probe casing. The upper end of the tube is fitted with a rubber stopper which has three larger holes and one small hole. The larger holes are for three electrodes, namely, a saturated calomel reference electrode, a glass pH electrode, and a platinum oxidation

potential electrode. Each electrode has a 10-foot lead wire to allow easy setting of the potentiometer in a restricted underground space. The potential difference between the calomel electrode and the glass electrode gives the pH value of water, whereas that between the calomel electrode and the platinum electrode gives the oxidation potential. The small hole is fitted with a glass tube to which a rubber tube with a steel stop-cock is attached. This tube provides an outlet for the water that seeps into the probe from the other end of the casing.

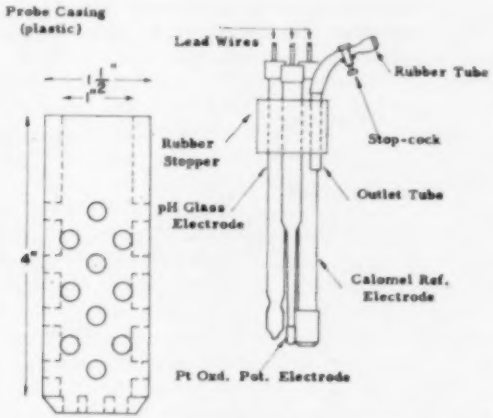


FIG. 1. The structure of the electrode probe used for Eh-pH measurements of natural waters.

The standard procedure for the measurement is to locate water seepage from the wall rock and to make a hole large enough to accommodate the probe in a direction very slightly dipping into the wall rock. In many cases, however, horizontal diamond drill holes were used. To prevent leakage of water and contamination by atmospheric oxygen, the gap between the hole and the probe was sealed with plastic modeling clay (mixture of wax and clay) at the mouth of the hole, as shown in Figure 2. In case the amount of water was not sufficient to fill up a hole, or the seepage was only from the roof, a plastic vessel was used to collect the water and the probe was dipped into the vessel as a substitute method. Such a method, however, is not adequate for deep-circulating water unless the rate of drip is fairly rapid and the measurement is made immediately, as the rate of change of oxidation potential of a dilute solution due to exposure to atmospheric oxygen is remarkable in a low potential region. This point was demonstrated in laboratory experiments to be described later.

The portable potentiometer used in the present study is a Beckman N-2 pH meter. This pH meter is essentially a vacuum-tube voltmeter with very high input impedance and sensitivity. With a platinum electrode instead of

a glass electrode, it gives the oxidation potential of a solution with reference to a saturated calomel electrode within a range of ± 420 mv. As the meter is scaled in terms of pH, the reading has to be converted to the millivolt scale according to a formula provided by the maker. The Eh value (oxidation potential in terms of hydrogen scale) is calculated by adding 242 mv to the potential value thus obtained. For a potential higher than 420 mv, a portable null-point type potentiometer was used as an auxiliary instrument. Temperature compensation is necessary for the pH measurement. The temperature of water was read with a mercury thermometer and the temperature compensator of the pH meter was adjusted accordingly. Since underground humidity is sometimes exceedingly high, extreme caution had to be taken to keep the electronic instruments dry.

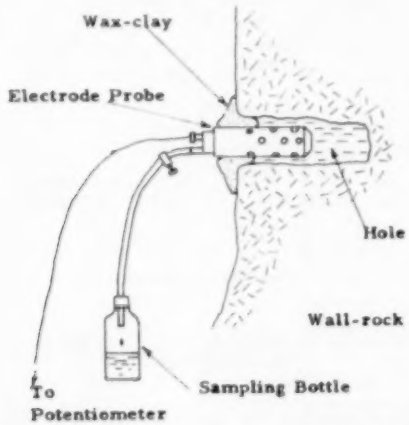


FIG. 2. A method of plugging the electrode probe into wall-rocks.

*Contamination Problem.*—In the course of planning the field Eh and pH measurements, serious questions had been raised as to whether the process of mining might invalidate the data obtained using above method. The most serious cause of possible deviation from an undisturbed, natural condition is the contamination by atmospheric oxygen introduced as the result of underground mining operations, with a subsequent rise in oxidation potential. Complete elimination of the oxygen contamination is next to impossible, for we have no direct access to depth without some sort of mining operations. This situation is not hopeless, however, since oxygen contamination always tends to result in a measured value of the oxidation potential higher than the one that would have been read if no contamination had taken place. It is a very plausible assumption that the true oxidation potential is not higher than the measured potential. We can apply the criterion, therefore, that the measured potential gives the upper limit for the true oxidation potential prevailing at depth. Other possibilities for contamination include mixing

of introduced water and contact with the materials used in mining operations. These contaminations, however, do not present any serious problem, for they can be eliminated with suitable precautions.

### *Field Results*

*Magma Mine, Superior, Ariz.*—Descriptions of the geology and mineralogy of the Magma deposits were given by Browning and Snow (7), Short and Ettlinger (51), Ettlinger and Short (17), Short and Wilson (52), and Short et al. (53), the last paper being the most complete reference. Copper is the principal ore metal of the mine. The dominant ore minerals are pyrite, bornite, chalcopyrite, and enargite. Tennantite and hypogene chalcocite occur in subordinate amounts. The outcrops do not show strong gossans. Carbonates of copper with a relatively small amount of iron oxide are found at a depth about 100 feet below the surface. Supergene enrichment is important in the Main vein above the 800 level. In the western portion of the mine, the bottom of the oxidized zone is nearly horizontal. In the eastern portion, on the other hand, the lower limit of the oxidized zone is roughly parallel to inclined sedimentary beds, oxidized ores appearing even below the 800 level. Short et al. (53) suggested the possible superposition of two stages of oxidation to account for this bending of the bottom of oxidation. The ground water table stood at about the 400 level in the No. 1 shaft before the start of the extensive mining operations. At present, water is seeping into the 500 level at the bottom of the Martin limestone between No. 1 and No. 4 shafts. The seepages of a considerable amount of water is limited to the 2,550 level and below in the eastern section, and the 4,800 level in the western section. In those places, drill holes provided the best source of natural water.

The data for the 15 measurements of Eh and pH values of natural waters at the Magma mine are listed in Table 1. The measurements from M-1 through M-8 were made in the primary ore zone, where the sulfide minerals are free of oxidation. The measurements M-1, M-2, M-3, M-4, M-6, and M-7 were made in horizontal drill holes where water seepages were abundant. These measurements gave the lowest oxidation potential values, indicating the least degree of oxygen contamination. Measurements M-3 and M-4, which were made in the vicinity of the North Branch vein, gave comparatively high potential values among the measurements made in drill holes. The measurement M-5 was made through the standard procedure described previously. The water seepage was meager, hence the possibility of oxygen contamination was high. Measurement M-8 was made by collecting water drips from the wall into a plastic vessel. There was little doubt about the oxygen contamination in this case. Measurements from M-9 through M-15 were made in the zone of oxidation, where the ores had been oxidized. A considerable amount of organic matter was present in the small water sump where measurement M-11 was made. Some live weeds were also present. The reducing action of organic matter appears to be responsible for the relatively low Eh value obtained in this measurement.

TABLE 1—Eh–pH Values of Natural Waters in Mining Districts

| Measurement number | Location | Level | pH | Eh (V) | (°C) | Method | Zone | Descriptions |
|---|---|---|---|---|---|---|---|---|
| (1) Magma Mine, Superior, Arizona | | | | | | | | |
| M-1 | West | 4,800 | 7.8 | 0.10 | 67 | DDH | P | Barren Pinal schist, no sulfide. |
| M-2 | West | 4,800 | 7.7 | 0.10 | 59 | DDH | P | Barren Pinal schist, no sulfide. |
| M-3 | West | 4,800 | 7.4 | 0.24 | 68 | DDH | P | North Branch vein, altered Pinal schist & sulfides. |
| M-4 | West | 4,800 | 6.3 | 0.26 | 46 | DDH | P | North Branch vein, altered Pinal schist & sulfides. |
| M-5 | East | 2,800 | 8.0 | 0.32 | 42 | STD | P | Barren quartzite, 10 feet below the contact with limestone. |
| M-6 | East | 2,800 | 8.5 | 0.14 | 40 | DDH | P | Mineralized limestone, hole through the ore body. |
| M-7 | East | 2,550 | 8.6 | 0.12 | 45 | DDH | P | Barren limestone, no sulfide. |
| M-8 | East | 2,550 | 6.2 | 0.31 | 36 | DCV | P | Long-exposed, barren diabase sill. |
| M-9 | Central | 500 | 8.1 | 0.35 | 22 | DCV | O | Martin limestone-Troy quartzite contact, barren. |
| M-10 | Central | 500 | 7.7 | 0.38 | 21 | STD | O | Clay at the contact of Martin limestone and Troy quartzite. |
| M-11 | Central | — | 4.6 | 0.30 | 26 | DRT | O | Small sump near an outcrop, organic matter abundant. |
| M-12 | Central | — | 5.1 | 0.51 | 29 | DRT | O | Outcrop, limestone stained with Fe and Mn oxides. |
| M-13 | Central | — | 4.4 | 0.57 | 29 | DRT | O | Outcrop, limonitic soil. |
| M-14 | Central | — | 4.6 | 0.45 | 28 | DRT | O | Outcrop, weathered and bleached shale. |
| M-15 | Central | — | 5.4 | 0.43 | 27 | DRT | O | Outcrop, rain-water sump with organic matters. |
| (2) San Manuel Mine, San Manuel, Arizona | | | | | | | | |
| S-1 | North | 1,475 | 8.5 | 0.15 | 31 | STD | P | Quartz monzonite porphyry with disseminated sulfides. |
| S-2a | North | 1,475 | 8.5 | 0.20 | 29 | DCV | P | Quartz monzonite porphyry with sulfides, ore grade. |
| S-2b | North | 1,475 | 8.3 | 0.07 | 31 | STD | P | Quartz monzonite porphyry with sulfides, ore grade. |
| S-3 | Haulage drift | 1,475 | 6.2 | 0.27 | 30 | STD | P | Quartz monzonite, barren. |
| S-4 | North drift | 1,475 | 5.6 | 0.23 | 28 | STD | P | Quartz monzonite, barren. |
| S-5 | South | 1,415 | 6.0 | 0.37 | 27 | DCV | (O) | Quartz monzonite, water from a churn drill hole. |
| S-6 | Main | 1,475 | 5.7 | 0.20 | 28 | DCV | P | Main ore body, mineralized porphyry. |
| S-7 | Main | 2,075 | 8.7 | 0.14 | 33 | STD | P | Quartz monzonite with sulfides, newly opened drift. |
| S-8 | Main | 2,075 | 8.4 | 0.13 | 33 | DDH | P | Quartz monzonite with sulfides, newly opened drift. |
| S-9 | Main | 2,075 | 8.5 | 0.17 | 33 | STD | P | Quartz monzonite with sulfides. |
| S-10 | Main | 2,075 | 8.6 | 0.15 | 33 | DDH | P | Quartz monzonite porphyry with sulfides, newly opened drift. |
| S-11 | Main | 2,075 | 8.4 | 0.15 | 33 | STD | P | Pyritized quartz monzonite porphyry, abundant water, West Branch drift. |
| S-12 | Main | 2,075 | 8.6 | 0.08 | 33 | DDH | P | Pyritized quartz monzonite, West Branch drift. |
| S-13 | | — | 7.6 | 0.40 | — | DRT | O | Surface water sump, abundant limonite. |
| (3) Cole and Campbell Mines, Bisbee, Arizona | | | | | | | | |
| B-1 | Cole, 119 x-cut | 800 | 7.9 | 0.23 | 23 | DDH | O | Limestone laminated with shale. |
| B-2 | Cole, 155 Raise | 900 | 7.5 | 0.22 | 22 | STD | O | Limestone, no sulfide. |
| B-3 | Cole, 120 x-cut | 800 | 8.3 | 0.34 | 22 | DCV | O | Oxidized ore in limestone. |
| B-4 | Cole, 67 x-cut | 600 | 7.9 | 0.34 | 24 | DCV | O | Oxidized ores in limestone, adjacent to enriched ores. |
| B-5 | Campbell, 56 x-cut | 2,800 | 8.0 | 0.13 | 31 | DCV | P | Limestone, adjacent to a primary ore body. |
| B-6 | Campbell, 11 x-cut | 2,800 | 7.8 | 0.11 | 30 | DCV | P | Silicified limestone. |
| B-7 | Lavender Pit | — | 2.5 | 0.70 | 26 | DRT | O | Surface water sump, brownish blue color because of Fe and Cu. |
| B-8 | Leaching Plant | — | 2.2 | 0.69 | 27 | DRT | O | Head liquor of copper ppt. plant. |
| (4) Continental No. 1 Mine, San Juan County, Utah | | | | | | | | |
| C-1 | C-24 | 150' | 8.4 | 0.27 | 15 | DCV | (O) | Water migrates down through a drill hole, U-bearing quartz sandstone. |
| C-2 | C-45 | 100' | 8.1 | 0.21 | 13 | DCV | P | Calcareous sandstone with low-grade U-ores, abundant disseminated pyrite. |
| C-3 | C-5 | 100' | 8.3 | 0.13 | 12 | STD | P | Carbonaceous, calcareous sandstone with about 1% uraninite. |
| C-4 | C-41 | 250' | 8.7 | 0.18 | 12 | STD | P | Fine shale below U-bearing Moss Back sandstone. |
| C-5 | C-29 | 250' | 8.5 | 0.09 | 13 | DCV | P | U-bearing Moss Back sandstone. |
| C-6 | — | 0 | 8.3 | 0.28 | — | DRT | O | Surface soil near the Divide mine, sampled at the bottom of a gulch. |

P: Primary ore zone; O: Oxidized ore zone; STD: Standard method; DDH: Diamond drill hole; DCV: Drips collected in a vessel; DRT: Direct contact.

*San Manuel Mine, San Manuel, Ariz.*—The geology of the San Manuel deposit, Ariz., was described by Schwartz (50). The ore body is composed of chalcopyrite and pyrite, disseminated through quartz monzonite, monzonite porphyry, and diabase. Supergene oxidation and enrichment of the deposit have been extensive. The depth of oxidation ranges from 285 to 1,630 feet over a wide area. An irregular supergene sulfide zone is present below the oxidized ore. The zones of oxidation and enrichment are not related to the present erosion surface and water table. Schwartz (50) concluded that they were developed during an earlier cycle of erosion. The water table stood at depths of 300 to 800 feet before extensive mining operations began. Drainage by the mining operations lowered the water table and the amount of water seepage has been reduced to occasional drips along the south fringe drift of the main ore body at the 1,415 level. Abundant water was encountered in the new drifts around the north ore body at the 1,475 level and along the cross-cut from No. 1 shaft to the main ore body at the 2,075 level.

The data for the 13 measurements of Eh and pH values of natural waters at the San Manuel mine are listed in Table 1. The method of measurement applied for each measurement is also noted in the table. The measurements from S-1 through S-12 were made in the primary ore zone. Measurement S-5 was made with water coming out of a churn drill hole which had been sunk from the surface. Although the measurement was made within the primary ore zone, the result of the measurement should be considered to represent the Eh and pH conditions for the zone of oxidation, since the water was probably coming from the surface zone directly. The results of measurements S-2a and S-2b are interesting in that these results indicate the difference in the extent of oxygen contamination, depending on the method of measurement used. The two measurements were made at the same location, but by different methods. Abundant water was coming out of the wall of a newly opened drift at the location. S-2b was made through the standard procedure in which the electrode probe was plugged into a hole cut into the wall rock, whereas S-2a was made by dipping the electrode probe into the water collected in a plastic vessel. Although S-2a was made within a few minutes after the seeping water was collected in the vessel, the measured oxidation potential in this case was 0.13 volt higher than the case of S-2b, indicating the rapidity of the change of oxidation potential of natural water in the primary ore zone upon exposure to atmospheric oxygen. Measurement S-13 was made at a surface water sump at the site of a new open-pit mining operation where the surface soil had been removed recently. Limonite was abundant in the sump.

*Cole and Campbell Mines, Bisbee, Ariz.*—The geology and ore deposits of Bisbee area, Ariz., were described by Ransome (46), Notman (42), De Kalb (14), Tenney (58, 59, 60), and Bateman (4). Some 5,000 feet of Paleozoic limestones and quartzites overlie Precambrian Pinal schist. Their eroded surface is overlain by 4,000 to 5,000 feet of Cretaceous sediments bottomed by the Glance conglomerate. A stock, dikes, and sills of quartz monzonite to granite porphyry and of late Cretaceous or early Tertiary age, intrude the sediments. The mineralization is closely associated with this igneous activity.

Within the limestone the deposits are beds or pipes of massive sulfide replacement, whereas within the porphyry they are disseminated replacements. The primary ores have been deeply oxidized and developed into rich supergene sulfide ores below the oxidized zone. The present water table does not correspond to the bottom of the oxidized zone. The valley filling in the adjacent Sulphur Springs Valley caused a rise in the water table with drowning of oxidized ores. Locally, supergene sulfide bodies persist above the water table, because of an arid climate. Gossans enclose bodies of oxidized ores and cap the ore bodies.

The data for the 8 measurements of Eh and pH values of natural waters at the Bisbee district are listed in Table 1. The measurements from B-1 through B-4 were made at the upper levels of the Cole mine, where the primary sulfides had been oxidized or undergone supergene replacement. The measurement B-4 was made with the water that seeped through oxidized ores. Supergene enriched ores, however, were exposed along the same drift away from the seepage. Measurement B-5 was made on water that was gushing out at a rate of approximately one half gallon per minute from a fissure developed within limestone. Precipitation of ferric hydroxide was observed at the mouth of the fissure, indicating active oxidation of dissolved ferrous iron species as the result of exposure to atmospheric oxygen. Measurement B-7 was made with the water that had been pooled in a water sump at the bottom of the Lavender pit. The color of the water was brownish blue owing to the high concentrations of copper and iron. Measurement B-8 was made on the head liquor for cement copper recovery which had been sprayed over a low-grade ore dump. The Eh and pH values for the last two measurements may represent those that prevail in the zone of intense oxidation where sulfide minerals are actively oxidized.

*Continental No. 1 Mine, San Juan County, Utah.*—The Continental No. 1 mine is located at the southern flank of the Lisbon Valley anticline in San Juan County, Utah. The geology and uranium deposits of this area have been extensively studied by many geologists of the U. S. Atomic Energy Commission. Reference will be made to the papers by Dix (15), Isachsen (32), and Lekas and Dahl (40). The known sedimentary rocks that form the anticline range from Pennsylvanian to upper Cretaceous in age. The rocks exposed in the immediate vicinity of the Continental No. 1 mine are the Cutler formation of Permian-Pennsylvanian age, and the Chinle and the Wingate sandstone formations of upper Triasic age, which unconformably overlie the former. The uranium deposit occurs as tabular bodies within the lower 20 feet of the Moss Back member of the Chinle formation, which is characteristically gray-green in color. In the mine workings, the host rocks show abundance of carbonates and carbonaceous materials. Coalified woods are common. In places, fine-grained pyrite is abundant within the bleached sandstone layers, which total several inches in thickness. Pyrite nodules up to half an inch in diameter are common in both the bleached sandstone layers and the dark brown uranium ores. The abundant occurrence of pyrite is limited to the ore horizon of the Moss Back member. The ore horizon dips slightly southward at the end of the incline of the mine, which is sunk

westward at the southeastern rim of the Lisbon Valley and attains a depth of about 100 feet where it joins the main drift. The depth of the main drift gradually increases westward as the surface elevation rises from 6,550 feet to 6,780 feet above the sea level. The water table was quite close to the surface before mining operation started. At present, occasional seepage is observed in the older workings. Two ore bodies were being mined at the time of the survey, and water was fairly abundant at the newly developed western ore body.

The data for the 6 measurements of Eh and pH values of natural waters at the Continental No. 1 mine are listed in Table 1. The measurements from C-1 through C-5 were made along the uranium-bearing Moss Back sandstone. Although the sandstone member lies almost horizontally, the depths of the locations for the measurements vary according to the elevation of the surface, which increases toward west. The measurement C-1 was made with water that appeared to have come from the surface zone through a vertical drill hole. There was little doubt about the intense contamination of the water by atmospheric oxygen. The measurements C-2, C-3, and C-5 were made with water that was seeping out of small fissures developed within the uranium-bearing Moss Back quartzose sandstone, which is rich in carbonaceous materials and carbonates. Fine-grained pyrite crystals are locally abundant in the sandstone. Measurement C-4 was made with water that was coming out of fine clayey shale of the Cutler formation at a spot several inches below the contact with the Moss Back sandstone. Measurement C-6 was made with moist surface soil at the bottom of a small gulch near the Divide mine, which is located about a half mile west of the Continental No. 1 mine.

### *Discussion of Field Results*

The measured Eh and pH values of natural waters in the four mining districts described above are plotted in an Eh-pH diagram in Figure 3. The values obtained in the zone of oxidation are represented by crosses, and those in the primary sulfide zone by dots. Most of the values measured in the zone of oxidation fall on or somewhat above a line which was first drawn empirically on the diagram and was later found to coincide with the standard potential of the hydrogen peroxide-oxygen gas couple:

$$H_2O_2 = O_2 + 2H^+ + 2e, \quad Eh = 0.682 - 0.0591\ pH. \qquad (1)^1$$

[1] Any oxidation-reduction reaction may be split into two "half-cell reactions," or "couples," that indicate the mechanism by which the electrons are transferred from the reducing agent to the oxidizing agent. Such a couple may be represented by the following general equation:

$$aA + wH_2O = bB + mH^+ + ne.$$

The lower-case letters, except $e$, specify the mole numbers of the chemical species involved. The reduced species is indicated by $A$, the oxidized one by $B$, and electrons by $e$. The hydrogen gas-hydrogen ion couple is usually taken as the reference couple, its potential being defined as zero:

$$H_2 = 2H^+ + 2e, \quad \Delta F^\circ = 0, \quad \text{and} \quad E^\circ = 0.$$

The oxidation potential in this hydrogen scale is often called Eh. As proposed by Latimer (39) to rescue the current impasse regarding the convention of the electrode sign, the relationship of

It is a remarkable fact that the Eh and pH values measured in the oxidizing environment fall within a relatively narrow zone, despite the diverse conditions and localities of the measurements. The zone lies much below the upper limit of the stability field of water that represents the standard equilibrium potential between water and oxygen gas. The partial pressure of oxygen gas in air is approximately 0.2 atm. at the ground level, and the oxidation potential of a solution in contact with air for a long period of time should approach the potential given by the following equation, if it is a reversible one:

$$2H_2O = O_2 + 4H^+ + 4e, \quad Eh = 1.229 - 0.591\,pH + 0.0148 \log P_{O_2}$$
$$= 1.219 - 0.051\,pH. \qquad (2)$$

Even though some measurements were made in intensely oxidized surface environments, none of the results indicated that this equilibrium had ever been reached.

Examination of the results of other workers obtained from different environments also points to a similar conclusion. Allgeier, Hafford and Juday (1) measured the Eh and pH values *in situ* of the water and bottom

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the free energy change of the reaction, $\Delta F$, to the oxidation potential, Eh, of a couple may be expressed as:

$$Eh = \frac{\Delta F}{nf} \quad \text{where, } f = \text{Faraday } (= 96{,}500 \text{ Coulombs} = 23{,}070 \text{ cal/mole}).$$

Then, the Eh of the above couple is given in terms of the standard free energies of formation, activities, and mole numbers of involved species as:

$$Eh = \frac{b\Delta F_B^\circ - a\Delta F_A^\circ - w\Delta F_{H_2O}^\circ}{23{,}070\,n} - 0.0591 \frac{m}{n} pH + \frac{n}{0.0591} \log \frac{(B)^b}{(A)^a}.$$

If $n = 0$, the first equation represents an acid-base reaction, where $A$ is a proton-donor and $B$ a proton-acceptor:

$$aA + wH_2O = bB + mH^+.$$

At equilibrium and under standard conditions of $T$ and $P$, $-\Delta F^\circ = RT \ln K$ where $K$ is the equilibrium constant. Hence,

$$\log K = \frac{-\Delta F^\circ}{2.303RT} = \frac{a\Delta F^\circ + w\Delta F^\circ - b\Delta F^\circ}{1{,}363}.$$

Also:

$$K = \frac{(B)^b \cdot (H^+)^m}{(A)^a}$$

$$\log K = b \log(B) - a \log(A) - m\,pH.$$

Upon rearrangement,

$$pH = \frac{1}{m}\left[-\log K + b \log(B) - a \log(A)\right].$$

From the above equations, we get an expression for the equilibrium pH in terms of the free energies of formation and activities of the substances involved:

$$pH = \frac{1}{m}\left[\frac{b\Delta F_B^\circ - a\Delta F_A^\circ - w\Delta F_{H_2O}^\circ}{1{,}363} + b \log(B) - a \log(A)\right].$$

In this paper, rounded brackets denote activities of species, and square brackets concentrations. The values of free energy of formation used for the calculations of Eh and pH values are taken from Latimer (38), unless otherwise noted.

sediments of eleven lakes in Wisconsin, together with depth, temperature, and the amounts of dissolved oxygen, ferrous and ferric iron, and hydrogen sulfide. Their results are plotted on an Eh-pH diagram in Figure 4. Crosses

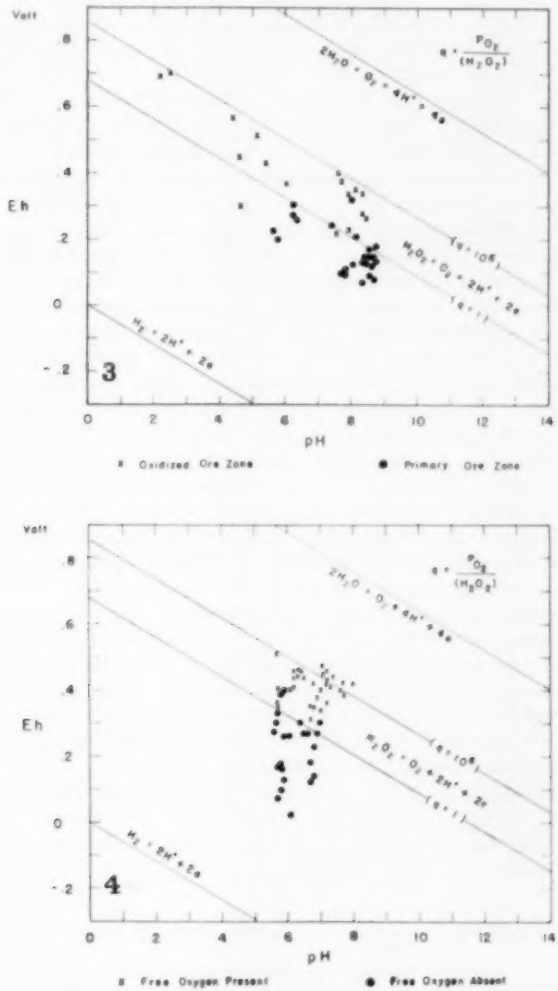


FIG. 3. Plots of Eh-pH values of natural waters in four mining districts. Circles represent measurements in the primary sulfide ore zone, and crosses those in the zone of oxidation.

FIG. 4. Plots of Eh-pH values of lake waters and of lake sediments in Wisconsin. Original data by Allgeier, Hafford, and Juday (1).

represent the values obtained in the near-surface zone where free oxygen is present, and dots those obtained in the deeper zone where oxygen is absent. The boundary between the two zones again appears to coincide with the standard potential of the hydrogen peroxide-oxygen gas couple. The values obtained in oxygenated zones also fall within a relatively narrow zone above this potential. In their study of water-logged soils, natural waters and muds, Pearsall and Mortimer (43) have called attention to the fact that relatively low concentration of oxygen suffices to maintain predominantly "oxidized" conditions. They indicate that the change-over from reducing to oxidizing conditions takes place at a value about 0.35 volt at pH of 5 in natural waters and that this has considerable ecological significance. At pH of 5, the hydrogen peroxide-oxygen gas couple gives a potential of 0.386 volt. The results of other measurements that were clearly made in oxygenated environments correspond more or less closely to the values already discussed.

The above results for oxygenated environments all indicate that: (1) the potentials observed are much lower than the potential that would be measured if a reversible equilibrium were established between oxygen and water, and (2) the Eh and pH values lie within a relatively narrow zone above the standard potential of the hydrogen peroxide-oxygen gas couple. The fact that the presence of dissolved oxygen in water is a common factor to those measurements strongly suggests that the control of the oxidation potential of an "oxidizing" environment is related to the reaction mechanism of oxygen reduction. This possibility is further supported by the fact that hydrogen peroxide is known to occur in the process of oxygen reduction.

The Eh and pH values measured in primary ore zones are generally lower than the line representing the standard oxidation potential of the $H_2O_2$-$O_2$ couple. It is difficult, however, to draw a definite conclusion as to the Eh-pH conditions prevailing at depth from the results of the field measurements alone. Oxygen contamination of the water is inevitable because of mining operations, measured Eh values becoming higher than the natural ones. The rate of Eh change of a dilute solution by oxygen contamination is very rapid, if the initial oxidation potential of the solution is much lower than the standard potential of the $H_2O_2$-$O_2$ couple, according to the results of experimental oxidation of iron and managanese solutions to be described later.

The acidity of water in the zone of oxidation ranges from 2.2 (leaching plant, Bisbee) to 8.3 pH units (800 Level, Cole mine, Bisbee), and that in the primary ore zone from 5.6 (1,475 Level, San Manuel mine) to 8.7 pH units (Continental No. 1 mine, Utah).

## EXPERIMENTAL OXIDATION OF METAL-SALT SOLUTIONS BY AIR

### *Method of Investigation*

The essential purpose of a series of experiments carried out was the observation of the rate of change in oxidation potential for a dilute metal-salt solution, while air was bubbled through the solution at a constant rate and temperature. Ferrous sulfate and manganous sulfate solutions were used,

for both iron and manganese are very common elements in the earth's crust and have more than one oxidation state within the stability range of water.

In each experiment, 200 cc of a 0.01 molal solution of ferrous sulfate or manganous sulfate was placed in an air-tight plastic cell. The cell is equipped with platinum, glass, and calomel electrodes, thermometer, burette, gas-bubbling tube, and an outlet tube which is connected to a gas trap. The solution was stirred throughout a run at a constant rate by means of a magnetic stirrer. The electrodes were connected to automatic potential recorders through preamplifiers. The solution was reduced with hydrogen gas prior to the introduction of air. After the solution was sufficiently

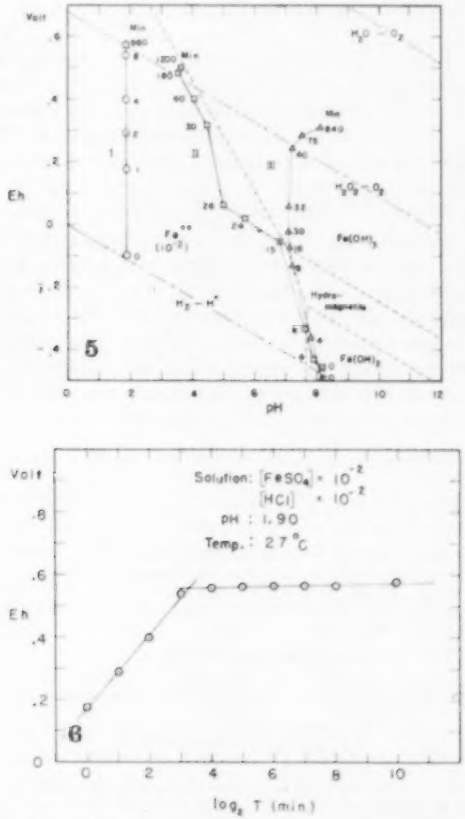


FIG. 5. The traces of the experimental runs on the oxidation of iron solutions by air.

FIG. 6. The plots of the Eh values against the logarithm of time in Run No. Fe-I, showing a sudden change in the rate of oxidation in the vicinity of the standard potential of the $H_2O_2$-$O_2$ couple.

reduced, either 1 N HCl or 1 N KOH solution was titrated from the burette to adjust the pH to a desired value. When both the oxidation potential and pH of the solution reached steady values, air was bubbled through the solution at a constant rate. The oxidation potential and pH values were recorded as functions of time of air-bubbling.

### *Experimental Results*

*Fe-$H_2O$ System.*—Of all the eight experimental runs with ferrous sulfate solutions, only three of them are discussed here. The other five runs gave similar results. The recorded time, Eh, and pH values for each run are presented on an Eh-pH diagram in Figure 5, which shows the progress of the runs.

In Run No. Fe-I, a 0.01 molal solution of ferrous sulfate was initially reduced with hydrogen gas, and then 2.0 cc of 1 N HCl solution was added (HCl 0.01 molal). The bubbling of hydrogen gas was continued during the addition of HCl. The Eh at the start of air-bubbling was –100 mv, reaching a constant value of 572 mv after 16 hours. The pH value remained constant at 1.90, and the temperature at 27° C. The result of the run is also plotted as Eh vs. time in Figure 6. The time of air-bubbling is taken as the abscissa on the basis of the exponent of 2. It is seen that the Eh changes linearly with the logarithm of time below 558 mv., at which value a sudden, distinct change in slope takes place in the trace of the Eh vs. log (Time) plots, indicating a change in the oxidation mechanism.[2] Above this potential, the change of Eh becomes vanishingly small. Although the plotted values above this potential are connected by means of a line on the diagram, the data could equally fit an asymptotic curve. A simple calculation shows that the $H_2O_2$-$O_2$ couple has a potential of 570 mv at pH = 1.9.

[2] The Eh value of the solution is given as a function of the activity ratio of ferric ion to ferrous ion as:

$$Fe^{++} = Fe^{+++} + \epsilon, \quad Eh = 0.771 + 0.0591 \log \frac{(Fe^{+++})}{(Fe^{++})}.$$

When the Eh is lower than about 0.6 volt, the iron in solution exists predominantly as ferrous ion, even though the activity coefficients for both iron species are taken into account. This permits the approximation of the ferrous ion concentration as equal to the total iron concentration, which is 0.01 molal in this run. Neglecting the activity coefficient for ferrous ion, the above potential equation may be rewritten as:

$$Eh = 0.879 + 0.591 \log (Fe^{+++}).$$

The change of Eh with the change of the logarithm of the concentration of ferric ion becomes:

$$\frac{d\,Eh}{d \log (Fe^{+++})} = 0.591 \text{ (constant)}.$$

Hence, a constant rate of production of ferric ion in the solution results in the change of Eh roughly proportional to the logarithm of time. The linearity of the plots of Eh vs. log(time) below the potential of 0.56 volt in Fig. 6 indicates this relationship. As the Eh becomes higher, the effect of the decrease in the ferrous concentration becomes significant, and the amount of Eh change for an equal increment of log(time) is expected to increase, provided the rate of formation of ferric ion remains constant. The drastic decrease in the slope of the Eh vs. log(time) plots above 0.56 volt is contradictory to this prediction. The discrepancy may be best explained by assuming a change in the oxidation mechanism.

In Run No. Fe-II, a 0.01 molal solution of ferrous sulfate was initially reduced with hydrogen gas. Then 4.0 cc of 1 N KOH solution was added to 200 cc of the solution. A white colloidal suspension of ferrous hydroxide was formed. After Eh and pH of the solution reached constant values, air was introduced. The white color of the ferrous hydroxide immediately changed to greenish blue, then to dark green, and further to black, indicating the formation of hydro-magnetite. Following the formation of hydro-magnetite, the Eh of the solution rapidly rose until it reached the value of –56 mv (pH = 6.80), where a brownish tint began to appear, indicating the formation of ferric hydroxide. The Eh-pH value shifted slowly along a line with the slope of 0.059 volt per pH (hydromagnetite-ferric hydroxide couple) until the entire hydromagnetite changed over to yellowish brown ferric hydroxide at a potential of +60 mv. Then the potential abruptly jumped to 305 mv (pH = 4.50) and very slowly proceeded along a line roughly parallel to the potential line of the ferrous ion-ferric hydroxide couple, which corresponds to:

$$Fe^{++} + 3H_2O = Fe(OH)_3 + 3H^+ + e,$$

$$Eh = 1.057 - 0.1773\,pH - 0.0591 \log(Fe^{++}). \qquad (3)$$

When the Eh of the solution reached the potential of the $H_2O_2$-$O_2$ couple at Eh = 470 mv and pH = 3.50, again the rate of the Eh change suddenly diminished. After 20 hours of continuous air-bubbling, the Eh remained constant at 500 mv with the pH equal to 3.68. This result indicates that a change in the oxidation mechanism takes place at the potential of the $H_2O_2$-$O_2$ couple regardless of the form of iron present in the solution, or whether the system is homogeneous or heterogeneous. It also indicates, however, that the presence of a solid phase of iron produces a marked dependency of the pH value of an iron solution upon the oxidation potential of the solution. Without adding any extra "free acid," the pH value of an initially neutral ferrous ion solution may become as low as 3 upon exposure to air.

Run Fe-III was made to examine the effect of the presence of a buffer agent. $CaCO_3$ was used as the buffer agent. 200 cc of a 0.01 molal $FeSO_4$ solution was reduced with hydrogen gas and then 1 gram of chemically precipitated $CaCO_3$ (analytical grade) was added together with 2.0 cc of 1 N KOH solution. When the mixture came into equilibrium, air was bubbled through. The color of the solution immediately changed from bluish white to dark greenish black. The Eh of the solution rapidly rose from –510 mv (pH = 8.20) to –85 mv (pH = 7.10), where yellowish brown ferric hydroxide began to form. When the hydromagnetite had completely changed to ferric hydroxide at Eh = +60 mv and pH = 7.10, the Eh again moved up fairly rapidly until it reached the potential of the $H_2O_2$-$O_2$ couple at Eh = 245 mv and pH = 7.22. After 14 hours of continuous air-bubbling the Eh remained almost constant at 310 mv and the pH at 8.10. Although the Eh value at the end of the run was slightly higher than the standard potential of the $H_2O_2$-$O_2$ couple, the fundamental mechanism of Eh-control appeared little affected by the presence of a buffer agent. There were slight variations in

pH during the run. It varied from the initial value of 8.20 to a minimum value of 7.10, and then back to 8.10 in the final stage. Probably the acid-base reaction:

$$CaCO_3 + H^+ = Ca^{++} + HCO_3^-$$

could not quite compensate for the acidification due to the reaction:

$$Fe^{++} + SO_4^{--} + 3H_2O = Fe(OH)_3 + SO_4^{--} + 3H^+ + e$$

during the active oxidation stage.

*Mn-$H_2O$ System.*—Seven runs were made with manganese sulfate solutions. Only the results of four typical ones are discussed here. The experimental data for the first three runs are plotted on an Eh-pH diagram in Figure 7. Most of the experimental procedures and conditions were the same as for the Fe-$H_2O$ system.

In Run Mn-I, a 0.01 molal $MnSO_4$ solution was reduced with hydrogen gas. The reduction was continued during and after the addition of 2.0 cc of 1 N $H_2SO_4$ solution until the Eh of the solution became almost constant at –36 mv. Following this, air was bubbled through the solution at a constant rate. After 20 hours of continuous air bubbling, the Eh reached a constant value of 639 mv. The pH remained constant at 2.10 throughout the run. The temperature was kept constant at 25° C. There was no visible change in the appearance of the solution. Apparently manganese dioxide did not form. As in the case of Run No. Fe-I, the data are plotted on an Eh-Time diagram (Fig. 8). A distinct change in the slope of the line is seen at a potential of 582 mv, which is very close to the potential of the $H_2O_2$ couple at this pH (558 mv at pH = 2.10).

In Run No. Mn-II, a pure 0.01 molal solution of $MnSO_4$ was used. Temperature was constant at 30° C from the start of the air-bubbling for about 5 hours. After 41 hours of continuous air-bubbling, the Eh reached 508 mv at pH = 4.07. The pH varied within the range of 4.07 to 4.11. There was no visible change in the appearance of the solution throughout the run. The above Eh value at the end of the run is slightly higher than the standard potential of the $H_2O_2$-$O_2$ couple which is 440 mv at pH = 4.10.

In Run No. Mn-III, 1.0 cc of 1 N KOH solution was added to 200 cc of 0.01 molal $MnSO_4$ solution after the latter was sufficiently reduced with hydrogen gas. White colloidal suspension of $Mn(OH)_2$ was formed. When both the Eh and pH of the solution became stable, air-bubbling was started. The Eh rapidly rose from the initial value of –210 mv to 200 mv, where beige-brown suspension, probably hydrohausmannite, began to form. The formation of the brown hydroxide was almost complete at 284 mv. During this portion of the run, the pH varied slightly from 9.17 to 9.40. After 21 hours of continuous air-bubbling, the potential reached 417 mv at pH = 6.45. The reason for the large shift of the pH from 9.40 to 6.45 in the late stage of the run is not clear. Probably disproportionation of the hydroxide had taken place during the run, producing a small amount of $Mn^{++}$ ions which established an equilibrium with the hydroxide. At a pH of 6.45, the $H_2O_2$-$O_2$

couple gives a potential of 301 mv. It is a general observation in the present series of experienments that the steady Eh values reached at the later stages of the runs tend to be more positive than the standard potential of the $H_2O_2$-$O_2$ couple at a higher pH range. A discussion of this fact will be given later.

The purpose of Run No. Mn-IV was to examine the effect of the variation of pH upon the Eh values of a Mn-$H_2O$ system containing solid phases of manganese. A solution containing 0.01 mole per liter each of $MnSO_4$ and KOH was oxidized by air until both the Eh and pH attained constant values. Then, pure nitrogen gas, which was completely deoxygenated by passing

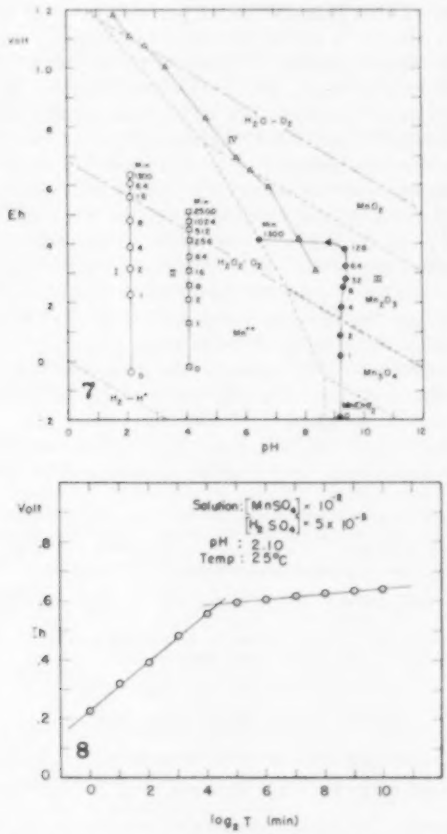


FIG. 7. The traces of the experimental runs on the oxidation of manganese solutions by air.

FIG. 8. The plots of the Eh values against the logarithm of time in Run No. Mn-I, showing a sudden change in the rate of oxidation in the vicinity of the standard potential of the $H_2O_2$-$O_2$ couple.

through a heated tube containing fine powder of metallic copper, was bubbled through the solution to expel the last trace of free oxygen present in the cell. The nitrogen bubbling was continued throughout the run to prevent the diffusion of free oxygen into the cell. After several hours of nitrogen bubbling the Eh and the pH values were constant at 310 mv and 8.40, respectively. At this stage, 1 N HCl solution was added from a burette. The recorded pH and Eh values are represented by the trace IV of Figure 7. The solution contained a brown suspension at the beginning of the acidification. The color gradually changed to dark brown and further to black as the addition of HCl proceeded. At the end of the run, the pH was lowered to 1.52 and the Eh reached a value of 1,180 mv. This potential is far higher than any potential obtained in other runs. It should be noted that hydrochloric acid is not an oxidizing agent, and yet the simple addition of this acid raised the Eh to a high value.[3] Important aspects of this result are that, when an aqueous system contains one or more solid phases, it is possible (1) to change the oxidation potential by simple acidification or basification, without adding an oxidizing or reducing agent; and (2) to raise the oxidation potential above the values usually obtainable through oxidation by air, by means of acidification. Another aspect, which is also related to the results of the previous runs, is that a direct oxidation of a manganous solution by air can not precipitate manganese dioxide in an acid environment. Either the acidification of an intermediate oxide or hydroxide which forms only in a basic environment, or some organic activity is probably required to precipitate the dioxide. This aspect is significant in connection with the geochemical separation of manganese from iron in a weathering environment. Krauskopf (35) discusses this problem extensively with some experimental results, and concludes that the preferential precipitation of iron under oxidizing conditions plays an important role in the separation. The above observational data strongly support his conclusion; within the normal pH range of the weathering environment, namely 4 to 6, dissolved ferrous

[3] The reason for this Eh change without the action of an oxidizing agent is explained in the following way. The Eh of a solution is determined by a reversible oxidation-reduction equilibrium of chemical species present in the solution. If $Mn^{++}$ ion and $Mn_3O_4$ exist in a solution, the Eh value is given as the function of both pH and $Mn^{++}$ ion activity, as

$$3Mn^{++} + 4H_2O = Mn_3O_4 + 8H^+ + 2e, \quad Eh = 1.824 - 0.2364\ pH - 0.0886 \log(Mn^{++}).$$

The Eh value increases as the acidity is increased. If sufficient acid is added to the solution, the following disproportionation reactions take place successively:

$$Mn_3O_4 + 2H^+ = Mn_2O_3 + Mn^{++} + H_2O,$$

$$Mn_2O_3 + 2H^+ = MnO_2 + Mn^{++} + H_2O.$$

When the first reaction occurs, the Eh is given by the equation:

$$2Mn^{++} + 3H_2O = Mn_2O_3 + 6H^+ + 2e, \quad Eh = 1.443 - 0.1773\ pH - 0.0891 \log(Mn^{++}).$$

If the second reaction takes place with increasing acidity, then we have only $Mn^{++}$ ion and $MnO_2$ and the Eh is given by

$$Mn^{++} + 2H_2O = MnO_2 + 4H^+ + 2e, \quad Eh = 1.228 - 0.1182\ pH - 0.0295 \log(Mn^{++}).$$

Hence, we have a high Eh value by simple acidification. The above disproportionation mechanism is probably important for the formation of manganese dioxide minerals in nature.

iron is easily precipitated as ferric hydroxide by atmospheric oxidation, whereas dissolved manganous ion remains in solution without being oxidized to one of the insoluble oxides or hydroxides.

## THEORETICAL CONSIDERATIONS

### *Oxidation Potential Control by Oxygen*

*Mechanism of Oxygen Reduction.*—The oxidation potential at which oxygen is reduced to water is given by the equation:

$$2H_2O = O_2 + 4H^+ + 4e, \quad Eh = 1.229 - 0.0591\ pH + 0.0148 \log P_{O_2}. \quad (4)$$

This is a relatively high potential among various known couples of inorganic substances. It predicts that oxygen should be a better oxidizing agent than perchlorate $ClO_4^-$ ion, if the above reaction is a reversible one. In reality, however, the reactions of oxygen at room temperature are often much slower than the reations of other oxidizing agents with less favorable potentials. It is even slower than ferric ion. This sluggishness of oxygen is due in part to the initial difficulty in breaking the bond between the two oxygen atoms. The faster reactions of oxygen are those in which the bond remains unbroken. According to Latimer (38), there is abundant proof that oxygen in the presence of hydrogen ion is generally reduced to hydrogen peroxide. The evidence of hydrogen peroxide forming as an intermediate product of oxygen reduction is not limited to aqueous solutions at room temperature, but also is found in numerous cases such as the thermal reaction of oxygen and hydrogen, autoxidation of biological systems and of metals, and electrolytic reduction of oxygen at a cathode. Reference will be made to a recent publication by Schumb, Satterfield, and Wentworth (49) as to an extensive review of the chemistry of hydrogen peroxide. The actual mechanisms involved in the process of reduction of oxygen in aqueous solution, however, has not been well established. In their study of the reactions of oxygen reduction at a mercury electrode, Iofa, Shimshelevich, and Andreeva (31) concluded that the reduction of oxygen to hydrogen peroxide was a first order reaction for oxygen in both acid and basic solutions. The reaction was postulated to proceed via $O_2^-$, $HO_2$, and $HO_2^-$, with the rate determined by the step:

$$O_2 + e \rightarrow O_2^-.$$

The reduction of hydrogen peroxide was also found to be a first order reaction. Latimer (38) states that with one electron reducing agents, $HO_2$ is an intermediate. The one electron steps in the reduction of $O_2$ to $2H_2O$ in acid solution proceed as indicated below:

$$O_2 \rightarrow HO_2 \rightarrow H_2O_2 \rightarrow H_2O + OH^- \rightarrow 2H_2O.$$

In an electrochemical study of the cathodic reduction of oxygen at platinum electrodes, Winkelmann (62) recently proposed a mechanism involving free

radicals:

$$\begin{array}{ccccccccccc} O_2 & \rightarrow & O_2^- & \rightarrow & HO_2 & \rightarrow & HO_2^- & \rightarrow & H_2O_2 & \rightarrow & OH + OH^- \rightarrow 2OH^-. \\ + & & + & & + & & + & & + & & \\ e & & H^+ & & e & & H^+ & & e & & \end{array}$$

Whatever the true mechanism may be, it appears to be a solidly established fact that hydrogen peroxide or its basic equivalent, peroxyl ion, is an intermediate product of oxygen reduction. From the fact that hydrogen peroxide is the most commonly detected intermediate product, it is apparently the most stable one among the intermediate products of oxygen reduction. It is not surprising, therefore, if the oxidation potential of an aqueous system in contact with free oxygen is controlled by the chemical behavior of hydrogen peroxide.

*Chemical Behavior of Hydrogen Peroxide.*—Hydrogen peroxide is one of the most powerful oxidizing agents in both acid and basic solutions. This is because of the high oxidation potential of the water-hydrogen peroxide couple:

$$\begin{aligned} 2H_2O &= H_2O_2 + 2H^+ + 2e, \\ Eh &= 1.772 - 0.0591\,pH + 0.0295\log(H_2O_2). \end{aligned} \tag{5}$$

It also behaves as a reducing agent against a moderately strong oxidizing agent, however, being itself oxidized to oxygen:

$$\begin{aligned} H_2O_2 &= O_2 + 2H^+ + 2e, \\ Eh &= 0.682 - 0.0591\,pH + 0.0295\log\frac{P_{O_2}}{(H_2O_2)}. \end{aligned} \tag{6}$$

The oxidation and reduction potentials of hydrogen peroxide are such that hydrogen peroxide should be able to oxidize itself, that is, it is thermodynamically unstable. It is unusually persistent with respect to disproportionation to water and oxygen. If a strong oxidizing agent is present in solution, however, a catalytic decomposition of the peroxide takes place. Consider the following potential in comparison with the two potentials of hydrogen peroxide given in equations (5) and (6):

$$\begin{aligned} Mn^{++} + 2H_2O &= MnO_2 + 4H^+ + 2e, \\ Eh &= 1.228 - 0.1182\,pH - 0.0295\log(Mn^{++}). \end{aligned} \tag{7}$$

We see that $H_2O_2$ should be able to oxidize $Mn^{++}$ to $MnO_2$, but should also be able to reduce $MnO_2$ to $Mn^{++}$, resulting in a catalytic decomposition of the peroxide. The decomposition of hydrogen peroxide by $Fe^{++}$ ion has first been shown to involve the free hydroxyl and perhydroxyl radicals, OH and $HO_2$, by Harber and Weiss (23, 24). The mechanism involved has been established by the work of Barb et al. (3), who have shown that the competition of ferrous ion and hydrogen peroxide for hydroxyl radical determines the extent of the generation of oxygen. The above relationship of the value of oxidation potential with the catalytic decomposition of hydrogen peroxide

is not limited to iron and manganese, but it generally holds true with couples whose potentials lie between the oxidation and the reduction potentials of hydrogen peroxide. In fact, a large number of elements have been found to be catalytic. The heavy and transition elements are particularly effective. Schumb et al. (49) give a periodic table showing the catalytic elements, which include Cr, W, Mn, Fe, Co, Ni, Cu, Ag, Au, Zn, Cd, Hg, Os, Ir, Pt, Pb, As, Bi, Br, and I. Even a trace concentration of such an element can decompose hydrogen peroxide.

*Mechanism of Oxidation Potential Control by Oxygen.*—From the foregoing discussions it may be seen that: (1) hydrogen peroxide generally forms as an intermediate product of oxygen reduction in aqueous solution; (2) hydrogen peroxide is unstable regardless of pH and catalytically decomposed by a couple whose potential lies between those of the oxidation and reduction potentials of the peroxide; and (3) many metal elements including iron and manganese actually catalyze the decomposition of the peroxide. An understanding of these facts makes it possible to explain the mechanism for the observed potential control, in natural environments and in experimental runs, of an aqueous system subjected to oxidation by free oxygen. Until the potential of the $H_2O_2$-$O_2$ couple is reached, ions in solution are quickly oxidized by the hydrogen peroxide produced from the oxygen reduction. When the oxidation potential of the solution exceeds that of the $H_2O_2$-$O_2$ couple, there are sufficient oxidizing agents present in the solution to oxidize the peroxide back to oxygen, counteracting further oxidation by the latter. The net effect thus becomes simply the decomposition of the hydrogen peroxide previously formed from oxygen. This means that oxygen is no longer available for further oxidation, though it may be abundant in the solution. So to speak, an "equilibrium" condition is established between oxygen and hydrogen peroxide due to the presence of catalytic agents. A reversibility is established in the $H_2O_2$-$O_2$ couple to control the oxidation potential of the solution. Iron and manganese, both effective catalysts of hydrogen peroxide decomposition, are common constituents of the earth's crust. This mechanism is, therefore, very likely to be operative in natural environments.

The problem of the deviation of the maximum Eh from the standard potential of the $H_2O_2$-$O_2$ couple with varying pH in the experimental runs seems to depend on the efficiency of the catalysis. If the oxidation of the peroxide proceeds more slowly than its reduction at the standard potential of the $H_2O_2$-$O_2$ couple, the oxidation potential of the solution may be raised considerably higher than this value, until sufficient amount of an oxidizing agent for hydrogen peroxide is produced. The Fh of the solution will stop at a potential where the rate of oxidation equals that of reduction for hydrogen peroxide. This rate factor must be considered where the rate of oxygen introduction is rapid and the oxidized form of the catalytic element is a solid. The rate of reaction is largely controlled by the frequency of collision, which would be much less for a solid phase than for an ionic species. At higher pH values the oxidized forms of both iron and manganese are solid, the fact which probably explains increasingly large upward deviation of the

final Eh values from the standard potential of the $H_2O_2$-$O_2$ couple with increase in pH observed in the experimental runs. In natural environments, however, this rate factor is probably insignificant, since the introduction of free oxygen to the deeper portion of the weathering zone is presumably very gradual. The Eh value would be determined mainly by the ratio of the activity of oxygen to that of hydrogen peroxide.

### *Oxidation Potential Control by Rock-Forming Minerals*

*Underground Waters at Depth.*—Underground waters at depth may originate through (1) penetration from above of meteoric water through soils and weathered rocks, and (2) preservation in situ or migration of primary water that was present at the time of formation of rocks. Meteoric water contains carbon dioxide and small amounts of dissolved substances derived from the atmosphere. Upon entering the soil and rocks, these react with the pre-existent minerals, forming new compounds that include carbonates, bicarbonates, and sulfates of alkali and alkaline earth metals, soluble alkali silicates, and free silica. By the time it reaches the level of the water table, the consumption of dissolved oxygen and the neutralization of acid components are nearly complete. The stagnant condition prevailing beneath the water table further accelerates the attainment of equilibrium between the water and the host rocks. Primary water, present in the host rocks at the time of deposition or intrusion, may also constitute part of the underground water. Connate water in a sedimentary rock is an example. Minor amounts of water are always liberated during magmatic activities. Such juvenile water may remain within the igneous rocks or permeate through overlying rocks, or migrate to the surface in hot springs and fumaroles. Primary water is presumably in equilibrium with the host rocks, so long as it exists in pore spaces and minute fractures of rocks for a geologic period of time. Regardless of origin, underground waters at depth are characterized by a prolonged contact with the host rocks. Their chemical nature is, therefore, largely influenced by the chemical and mineralogical composition of the host rocks.

Extensive discussions on the chemical composition of various waters are given by Clarke (12) and Rankama and Sahama (45). Recently, Schoeller (48) presented an extensive paper on the geochemistry of underground waters. Results of 50 analyses of mine waters were compiled by Hodge (26), and of 56 analyses by Emmons (16). Hodge (26) made comprehensive study of waters in mines of sulfide ores. Assuming that the balance between strong acids ($SO_4^{--}$, $Cl^-$) and alkalies determines the acidity of waters, he found that 22 were acid, 14 neutral, and 14 alkaline, among the 50 samples studied. All the acid waters were believed to be collected either in the zone of oxidation or not far below the ground water table, while the neutral and alkaline waters were mostly found at depths. He has shown with examples that, with increase in depth, (1) the acidity of waters decreases, (2) the concentration of salts of heavy metals decreases, and (3) the concentration of alkalies increases. The common cations found in these waters are those

of Ca, Mg, Na, K, Fe, Mn, Al, Zn, and Cu. $SiO_2$ predominates in alkaline waters. Sulfate, bicarbonate, and chloride ions are common anions.

Except for the zinc, copper, and sulfate ions, the common constituents of mine waters (particularly those from deep levels) are those of the average composition of the earth's crust, indicating the strong influence of the host rocks. Among the common elements in deep-circulating waters, iron and, to a lesser extent, manganese are most likely to be the elements that control the oxidation potential of the waters. This is because of the fact that their chemical species have oxidation-reduction couples whose potentials lie within the two stability limits of water. The alkali and alkaline earth elements have only one state of oxidation in this range. Sulfate ion can be reduced by bacterial action, but not through simple inorganic reactions in aqueous solution. It is highly probable, therefore, that iron is the most important element in controlling the oxidation potential of deep-circulating waters.

The Eh values of waters at depth, however, are not readily inferred from the ferric to ferrous iron ratios provided by chemical analyses of mine waters alone. As discussed previously, the Eh value of an iron solution depends upon the pH value as well as the presence of solid phases containing iron. In addition, the effect of mining operations must be considered, as in the case of direct Eh measurements with mine waters. Hodge (*26*) noted a few examples of oxygen contamination due to this cause. The present author observed in the mines of the Bisbee district that ferric hydroxide was actively precipitated from fresh waters coming out of drill holes. The precipitation was taking place along the walls a few feet below the holes. One approach to this problem might be to infer the Eh values for deep-circulating waters by assuming that (1) the waters are in equilibrium with their host rocks, (2) their Eh values are determined by the over-all equilibrium relationships among the chemical species of iron present in both the rocks and the solutions, and (3) the pH values are controlled by the mineralogical composition of the rocks.

*Oxidation Potential Control by Iron-rich Minerals.*—The iron in rocks generally exists in the forms of silicates, oxides, carbonates, and sulfides. Common host minerals for iron in igneous and metamorphic rocks include olivines, pyroxenes, amphiboles, micas, chlorites, magnetite, hamatite, ilmenite, pyrite and pyrrhotite. Iron-rich olivines are probably most reactive in oxidation reactions among the silicates. Fayalite forms goethite upon oxidation. Its oxidation potential may be given as:

$$Fe_2SiO_4 + 4H_2O = 2Fe(OH)_3 + SiO_2\ (\text{amorph.}) + 2H^+ + 2e,$$
$$Eh = 0.513 - 0.0591\ pH. \qquad (8)$$

So long as a solution is in contact with fresh fayalite, its oxidation potential must be equal to or below this value. Much more common than fayalite in diverse types of igneous and metamorphic rocks are iron oxides. Hematite is reduced to magnetite as:

$$2Fe_3O_4 + H_2O = 3Fe_2O_3 + 2H^+ + 2e, \quad Eh = 0.221 - 0.0591\ pH. \qquad (9)$$

The presence of hematite in unweathered rocks gives the lower limit for the Eh values of deep-circulating waters in contact with these rocks. The oxidation of magnetite to hematite may also take place at the above potential, if the reaction is reversible. The actual potential required for the oxidation of magnetite could be higher due to the reaction mechanism involved. In case both hematite and magnetite coexist in a rock, the Eh value of the solution long in contact with the rock would eventually approach the above value, the equilibrium with the two minerals being established. An interesting point with the potential of the magnetite-hematite couple is that most of iron-bearing silicates tend to establish this potential in the presence of water. (R. M. Garrels, oral communication). Upon hydrolysis the silicates should yield ferrous hydroxide, which would gradually convert to more stable magnetite plus hydrogen association with time.

In sedimentary rocks, siderite, hematite, goethite and iron sulfides are common host minerals for iron. Siderite oxidizes to ferric hydroxide at a potential given in the following equation:

$$FeCO_3 + 2H_2O = Fe(OH)_3 + CO_2 + H^+ + e,$$

$$Eh = 0.614 - 0.0591\ pH - 0.0591 \log P_{CO_2}. \qquad (10)$$

The potential is dependent on the partial pressure of carbon dioxide of the solution. Locally high partial prssure of carbon dioxide may exist at depth for various geologic and biogolical reasons. Near the water table, however, it could be reduced to a value close to that for the atmosphere at the ground level, namely $3 \times 10^{-4}$ atm. Substituting this value in the above potential equation, we get

$$Eh = 0.407 - 0.591\ pH. \qquad (10')$$

Siderite would be ultimately oxidized above this potential. Hence, the presence of fresh siderite in rocks at a depth not far below the water table is indicative of an Eh value equal to or lower than the potential given by equation (10'). The oxidation of iron sulfides will be discussed in a sister paper which will appear in this Journal, but it may be noted here that pyrite is not oxidized at a finite rate below the potential for the siderite-goethite couple under the atmospheric partial pressure of carbon dioxide. Some iron sulfides other than pyrite and marcasite may be oxidized below this potential, thus contributing to the control of the Eh values at depth. Their reaction mechanisms as well as compositions are not well understood; hence they are not considered in this paper.

### *Range of pH of Ground Waters*

The range of pH for the weathering environment is wide spread. According to Hawkes (26), the pH of the surface waters ranges from about 4.5 to 8.5, and that of soil lies between 4.0 and 9.0 In mining districts much lower pH values have been reported as the result of oxidation of sulfide minerals. A pH measurement for the sump water within a pit and for the

leaching water of an ore-dump, both in Bisbee district, gave the values 2.52 and 2.20, respectively. A pH value lower than 2 is very rarely reported, however. It is probably due to the fact that ferric hydroxide (limonite) generally remains in the oxidized zone until the last grain of pyrite is oxidized and consequently no more free sulfuric acid is produced, so that the pH is always controlled by the equilibrium relationship between the ferric hydroxide and ferrous or ferric ion in solution. Even when the entire iron in solution exists as ferric ion and its concentration is as high as 1 molal, the pH value cannot be lower than 1.6 so long as the ferric hydroxide is in contact with the solution as indicated below:

$$Fe(OH)_3 + 3H^+ = Fe^{+++} + 3H_2O, \quad pH = 1.614 - \tfrac{1}{3}\log(Fe^{+++}). \quad (11)$$

Even in an intensely oxidizing environment the activity of ferric ion rarely exceeds that of ferrous ion, so that the equilibrium pH values between ferric hydroxide and ground waters with dissolved iron would be better expressed by the equation:

$$Fe^{++} + 3H_2O = Fe(OH)_3 + 3H^+ + e,$$
$$pH = 5.96 - \tfrac{1}{3}\log(Fe^{++}) - 5.64\,Eh. \quad (12)$$

With the increase in both the concentration of dissolved iron and the oxidation potential the pH value decreases. Hodge (26) gives the value of 2.96 grams per liter as the average amount of total dissolved substances for acid mine waters, in which iron occupies 6 per cent in weight. This amount of dissolved iron corresponds to approximately $3.2 \times 10^{-3}$ molal concentration of ferrous ion. It suggests that 1 molal concentration of total iron would hardly be exceeded in natural waters.

A typical basic environment is that of a limestone area. The buffer action of calcite and carbon dioxide in natural environments have been discussed by Blumer (5), Hutchinson (29), and others. In the $CaCO_3$-$CO_2$-$H_2O$ system, the highest pH value is obtained when no external $CO_2$ pressure is applied. The dissolution of calcite in pure water builds up $CO_2$ pressure up to a certain value until equilibrium is reached. By using a method of successive approximation and taking $(Ca^{++})\ (CO_3^{--}) = 0.5 \times 10^{-8}$ and $k_2 = (H^+)\ (CO_3^{--})\ /\ (HCO_3^-) = 5 \times 10^{-11}$, Kolthoff and Stenger (35) gave the equilibrium concentration of hydroxl ion as $8.83 \times 10^{-6}$ mole per liter, which corresponds to the pH value of 9.95. Under the atmospheric partial pressure of $CO_2$, the equilibrium pH value is considerably lower. A simple approximation of the value may be made by assuming that most of $CO_2$ is dissolved as $HCO_3^-$ ion. In order to maintain electrical neutrality:

$$[H^+] + 2[Ca^{++}] = [OH^-] + 2[CO_3^{--}] + [HCO_3^-]. \quad (13)$$

As $[H^+]$, $[OH^-]$, and $[CO_3^{--}]$ are relatively small:

$$2[Ca^{++}] = [HCO_3^-] \quad (13')$$

$$CaCO_3 + H^+ = Ca^{++} + HCO_3^-, \quad K_a = \frac{(Ca^{++})(HCO_3^-)}{(H^+)},$$

$$\log K_a = 1.985, \quad (14)$$

$$CO_2 + H_2O = HCO_3^- + H^+, \quad K_b = \frac{(H^+)(HCO_3^-)}{P_{CO_2}}, \quad \log K_b = 7.80. \quad (15)$$

From (13′) and (14):

$$(HCO_3^-) = \sqrt{2K_a \cdot (H^+)}.$$

Substituting this value for bicarbonate ion in equation (15), we get

$$(H^+)^3 = \frac{K_b^2 \cdot P_{CO_2}}{2K_a},$$

$$\begin{aligned} pH &= \tfrac{1}{3}\left[\log 2 + \log K_a - 2\log K_b - 2\log P_{CO_2}\right] \\ &= 5.96 - \tfrac{1}{3}\log P_{CO_2}. \end{aligned} \quad (16)$$

Taking the value of $3 \times 10^{-4}$ for the partial pressure of $CO_2$ in the atmosphere at ground level, one obtains a pH value of 8.31 from the above equation. Where the atmosphere is in contact with moist rocks and soils containing calcite, the pH values are approximately equal to or below this value. Under ordinary natural environments, the pH values of ground waters are not likely to exceed that of pure water-calcite system, since calcite is very common constituent of rocks, soils, and gangues. Absence of calcite is usually due to the leaching by acids.

Hydrolysis equilibria of rock-forming silicate minerals could also contribute to the control of pH, particularly in the absence of carbon dioxide and carbonate ion species. Quantitative treatment of the acid-base reactions involving complex silicate minerals is very difficult, however, owing to the lack of knowledge on the hydrolysis mechanisms for these silicates. The work of Stevens and Carron (54) provides an empirical basis for inferring the pH range of deep-circulating waters. They measured the pH values of milky suspensions of minerals prepared by finely grinding the minerals in water. Such "abrasion pH" values for about 280 mineral species were determined. An inspection of their data indicates that the abrasion pH values of common rock-forming silicates mostly fall in the range between 6 and 10. Since deep underground waters are long in contact with these minerals, their pH values are normally expected to fall within this range.

## CONCLUSIONS

*Weathering Environment in Terms of Eh and pH.*—The field data, experimental results, and the mechanism of oxygen reduction all point to the conclusion that the oxidation potential of an aqueous system should be at or above the potential of the $H_2O_2$-$O_2$ couple so long as a detectable amount of free oxygen is present in the system. If the Eh of the system is below

this potential, oxygen whenever available would be immediately consumed in the oxidation of substances in the system, being itself reduced to hydrogen peroxide and further to water. When the Eh reaches the potential of the $H_2O_2$-$O_2$ couple, oxygen becomes compatible with the system so long as a trace of a catalyst of hydrogen peroxide decomposition is present, because now oxygen goes through the cycle $O_2 \rightarrow H_2O_2 \rightarrow O_2$. In this state, oxygen and hydrogen peroxide establishes a reversible equilibrium (metastable), and the ratio of the partial pressure of oxygen to the activity of hydrogen peroxide, together with pH, determines the Eh value of the system as shown by equation (6):

$$H_2O_2 = O_2 + 2H^+ + 2e, \quad Eh = 0.632 - 0.0591\ pH + 0.0295 \log \frac{P_{O_2}}{(H_2O_2)}.$$

The activity of hydrogen peroxide is presumably very small. At the bottom of the oxidized zone, most of the dissolved oxygen is consumed so that its partial pressure should be very small. It is unlikely, however, that the amount of unstable hydrogen peroxide ever exceeds that of the stable oxygen from which it is formed. The minimum ratio is very likely to be unity. Accordingly, the minimum Eh value for the weathering environment must be the standard potential of the $H_2O_2$-$O_2$ couple:

$$Eh^0 = 0.682 - 0.0591\ pH. \qquad (6^0)$$

At the surface, the partial pressure of oxygen is approximately 0.2 atm. The activity of hydrogen peroxide, on the other hand, is unknown except that it is probably very small. The ratio of former to latter is arbitrarily chosen as $10^6$ here. This gives the upper marginal value for the Eh of the weathering environment as written below:

$$Eh' = 0.859 - 0.0591\ pH. \qquad (6')$$

As already shown in Figures 3 and 4, most of the field data fall within the zone thus defined. Anomalously high values may be found very locally.

The pH range of the weathering environment is much more wide spread. The lowest pH values are usually found in mineralized areas where pyritic ores are actively oxidizing. The normal presence of goethite and limited concentration of dissolved iron in these areas indicates, however, that the pH value for the weathering environment would not be lower than the equilibrium pH value of a 1 molal solution of dissolved iron in contact with ferric hydroxide. At an Eh value close to the standard potential of the $H_2O_2$-$O_2$ couple the dissolved iron is predominantly ferrous ion activity-wise, and the lower marginal value of pH for the weathering environment may be expressed as:

$$Fe^{++} + 3H_2O = Fe(OH)_3 + 3H^+ + e, \quad pH^0 = 5.96 - 5.64\ Eh. \qquad (12^0)$$

The abundance of calcite usually accounts for high pH values in the weathering environment. Where rocks and soils are exposed to the atmosphere, the

pH values are not likely to exceed much the equilibrium pH value for the $CaCO_3$-$H_2O$ system under the atmospheric partial pressure of $CO_2$, which is about 8.3. Where air has a limited access and the consumption of $CO_2$ by organic activity or silicate hydrolysis is appreciable, higher pH values may be found locally. They are, however, very probably lower than the equilibrium pH value of the $CaCO_3$-$H_2O$ system without an external $CO_2$ partial pressure, which is approximately 10. This value may be taken as the upper marginal value of pH for the weathering environment.

*Depth Environment in Terms of Eh and pH.*—The term "depth environment" as used here refers to the environment of the portion of the earth's crust underlying the zone of weathering, being separated from the latter only by a thin layer of transitional nature. It is not intended to include zones of magmatic activity, but to refer to the zone where primary rock-forming and ore minerals remain intact from weathering processes. This environment is characterized by the practical absence of free oxygen, which indicates Eh values lower than the standard potential of the $H_2O_2$-$O_2$ couple. Because of the very restricted supply of free oxygen beneath the water table, which impedes the downward movement of oxygenated surface water, oxygen is no longer a major controller of Eh in this environment. It was discussed earlier that the Eh values of deep-circulating waters are probably controlled by their equilibrium relationship with iron-rich minerals in rocks. The common association of siderite and goethite in rocks, particularly in sediments, establishes a potential as a function of both pH and the $CO_2$ partial pressure. Considering the possibility of equilibration of the $CO_2$ partial pressure at a depth not far below the water table to that in the atmosphere, the presence of unoxidized siderite in the depth zone may be taken as the indication of Eh values equal to or below the following potential:

$$FeCO_3 + 2H_2O = Fe(OH)_3 + CO_2 + H^+ + e,$$
$$Eh' = 0.407 - 0.0591\ pH. \qquad (10')$$

This potential may be taken as the upper marginal value of Eh for the depth environment, assuming a steep potential gradient across a relatively thin layer of transitional character at the bottom of the zone of weathering, which probably directly underlies the water table. It may be noted here that the results of the electrochemical studies of oxidation of sulfide minerals, the discussion of which will appear in an accompanying paper in this Journal, are in agreement with this limit in that hypogene sulfide minerals can remain unoxidized below the potential thus defined.

In case of igneous and metamorphic rocks, the magnetite-hematite association is much more common. Although the magnetite-hematite couple is not unlikely to be a reversible one at low temperatures, a prolonged contact of deep circulating waters with both minerals tends to bring their Eh values close to the potential of this couple. The presence of iron-rich silicates also tends to establish the potential of the above couple, since hydrolyses of these minerals yield magnetite. In the sense that hematite is common in various types of rocks as well as in ore deposits, the potential at which hematite

is reduced:

$$2Fe_3O_4 + H_2O = 3Fe_2O_3 + 2H^+ + 2e, \quad Eh = 0.221 - 0.0591\,pH \quad (9)$$

may be taken as the lower marginal value of Eh for the depth environment. Anomalous low values may exist locally due to active reduction by $H_2$, $CH_4$, and other strong reducing agents produced during organic decomposition.

The same principles for defining the range of pH as those discussed for the weathering environment may apply to the depth environment, namely, the equilibrium pH value for the calcite-water system without an external $CO_2$

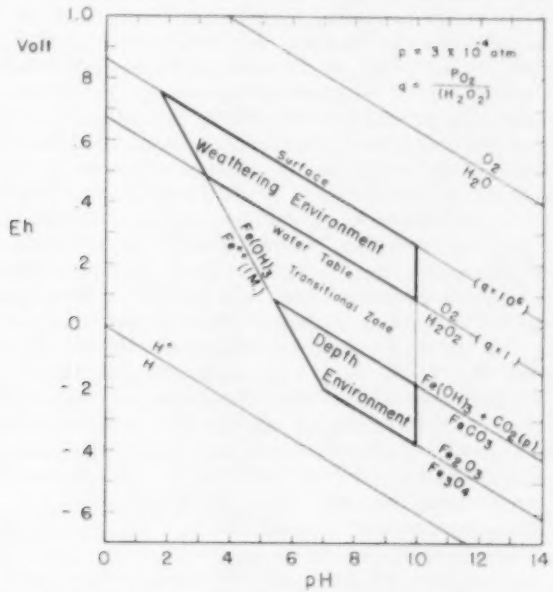


FIG. 9. The probable ranges of Eh-pH values for both the weathering environment and the depth environment.

pressure at the basic side, and that for the ferric hydroxide-ferrous ion (1 molal) system at the acidic side. The validity of the former is established by very common occurrence of calcite in various rocks. The latter is given as a function of Eh. Although equation (12°) is used to define the lower marginal value of pH for both environments, the equilibrium pH value for the depth environment as given by this equation is much higher because of more negative Eh value. The pH value at which the dissociation and oxidation of siderite take place simultaneously under a given partial pressure of $CO_2$ also corresponds to this value.

The marginal values of Eh and pH thus defined for both the weathering environment and the depth environment enclose two separate regions on a

Eh-pH diagram as shown in Figure 9. The region which lies in between the two on the diagram represents the environment of the transitional zone, which is probably the site for supergene enrichment of sulfide minerals.

## SUMMARY

The geochemical environment of a natural system can be described quantitatively in terms of oxidation potential and pH, without requiring consideration of all of the numerous chemical factors that exist in nature. In order to provide necessary field data for the study of geochemical environments of exposed sulfide ore bodies, field measurements *in situ* of Eh and pH values of natural waters surrounding ore bodies were carried out at four mining districts. The results in the zone of weathering indicate that the Eh and pH values for the weathering environment lie within a relatively narrow zone above the standard potential of the $H_2O_2$-$O_2$ couple. An experimental study on the oxidation of iron and manganese solutions by air showed a distinct change in the mechanism of oxidation, when the Eh values of the solutions reach the standard potential of the above cou le. Theoretical considerations of the mechanism of oxygen reduction and the chemical behavior of hydrogen peroxide provide a reasonable explanation for the above field and experimental observations. If oxygen gas is introduced into a solution that contains heavy metal elements in lower oxidation states, these chemical species are quickly oxidized by hydrogen peroxide which forms as an intermediate reduction product of oxygen. When the oxidation potential of the solution exceeds that of the $H_2O_2$-$O_2$ couple, the peroxide is catalytically decomposed by the heavy metal species. Oxygen becomes no longer available for further oxidation. Assuming an equilibrium condition, it is concluded that the value of oxidation potential for the weathering environment probably ranges between the standard potential of the $H_2O_2$-$O_2$ couple and the potential of the same couple taking the ratio of $P_{O_2} / (H_2O_2)$ equal to $10^6$.

The field measurements with deep-circulating waters did not produce conclusive results regarding the oxidation potential for the depth environment, except that the majority of the measured potentials are lower than the standard potential of the $H_2O_2$-$O_2$ couple. In many cases, there were strong indications that oxygen contamination due to mining operations might have affected the Eh values of the waters on which the measurements were made. An attempt was made to specify the range of oxidation potential for the depth environment from a consideration of the oxidation potentials of couples involving carbonate, hydroxides, and oxides of iron, iron being the most common element that occurs in more than one oxidation state in rocks. It is concluded that the value of oxidation potential for the depth environment probably ranges between the potential of the siderite-ferric hydroxide couple under the atmospheric partial pressure of carbon dioxide at the ground level and the potential of the magnetite-hematite couple.

From a consideration of the pH value at which goethite is dissolved and the average concentration of dissolved iron in mine waters, it is concluded that the equilibrium pH value for the $Fe(OH)_3$-$Fe^{++}$ (1M) system, which is

Eh dependent, may represent the lowermost value of pH for both the weathering environment and the depth environment. The fact that siderite in equilibrium with ferric hydroxide also dissolves at the pH value thus defined supports the validity of the above statement. Considering the very common occurrence of calcite in various rocks, the uppermost value of pH is taken as the equilibrium pH value for the calcite-water system without an external carbon dioxide partial pressure, which is approximately 10. This value also applies to both environments. The over-all relationships of the oxidation potential and pH conditions for the two environments are graphically presented above.

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LABORATORY OF MINING GEOLOGY,
HARVARD UNIVERSITY,
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# ORE CONTROLS IN THE MOROCOCHA DISTRICT, PERU[1]

R. H. NAGELL

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ABSTRACT

The Morococha mining district, 70 miles east of Lima, Peru, is a source of copper-silver-lead-zinc ores. Prospecting guides to ore are derived from an understanding of the complex structural history of the district during the Andean orogeny and the control exerted by geologic structure on the localization of ore bodies.

The stratigraphic section consists of the Permian Catalina volcanics and the Jurassic Potosi formation of limestone. Beginning in the Cretaceous and extending into the Tertiary, these rocks were folded, broken by thrust faults, brecciated, intruded by dioritic and quartz monzonite stocks, and cut by oblique fractures. Metasomatic alteration accompanied igneous intrusion and ore deposition.

Ore deposits in the forms of veins, contact pipes, and mantos are localized by the interacting effects of structural development which predates, and, to a small extent, post-dates, hydrothermal ore deposition. Ore shoots in veins are controlled by dilation of the vein walls, proximity to contacts of contrasting rock types, mineralogical zoning about centers of ore mineralization, and depth below the surface. Intrusive contacts, limestone alteration contacts, and intersecting fractures are the dominant controls on the localization of the contact pipe and manto ore bodies.

## INTRODUCTION

THE Morococha mining district is 92 miles by road east of Lima, Peru. Located immediately east of the continental divide (Fig. 1) formed by the

[1] Published with the permission of the Cerro de Pasco Corporation.

Andes mountains, the district ranges in altitude from 14,350 feet to 17,360 feet.

Several mining companies are producing copper, lead, zinc and silver ores within the 12 square mile area of the district. The greater part of the production is from the Cerro de Pasco Corporation's mines, particularly from the Morococha mine. This mine is served by four shafts and several adits and is developed to a depth of 1,700 feet.

Fig. 1.—Map of central Peru showing the location of the Morococha mining district.

## SUMMARY OF THE GEOLOGY

### *Stratigraphy*

The stratigraphic sequence at Morococha consists of a basement of Devonian (?) Excelsior phyllites and quartzites. This is overlain unconformably by the Permian Catalina volcanics. Disconformably overlying the Catalina volcanics is the Jurassic Potosi formation, which in turn is conformably overlain by the Cretaceous Santo Toribio formation of sandstone with intercalated basalts. The Santo Toribio formation grades upward into the Middle Cretaceous Machay limestone. The Machay limestone crops out at the borders of the district and is overlain by the Tertiary red beds. Table 1 summarizes the stratigraphic section at Morococha.

TABLE 1

STRATIGRAPHY OF THE MOROCOCHA DISTRICT

| Period | Formation | Lithology | Thickness |
|---|---|---|---|
| Cretaceous | Santo Toribio fm. (Goyllarisquisga fm.) | Sandstones, basalts | 1,500 feet |
| Jurassic | Potosi fm. (Pucara group) | Limestone, dolomite, shale, Montero basalt | 1,500 feet |
| Permian | Catalina volcanics (Yauli volcanics, Mitu group) | Dacite, rhyolite, andesite | 2,500 feet |
| Devonian(?) | Excelsior series | Phyllites, quartzites | — |

## *Structure*

The structural history of the district begins with the deformation and metamorphism of the Excelsior series prior to the formation of the Catalina volcanics. The Andean orogeny, beginning at the close of the Cretaceous and continuing through the Tertiary, further deformed the Excelsior series and left its imprint on the overlying Permian and Mesozoic rocks.

*Folding.*—In the Morococha region, folding during the Andean orogeny produced an elongate domal complex that strikes N 25° W in conformity with the general structural trend of the Andes in central Peru. The Morococha district is at the northern end of this domal complex.

*Thrust Faulting.*—North-striking thrust faults developed along with folding in the district. Two such faults, the Gertrudis thrust and the Potosi thrust, are known by their stratigraphic displacement. Other thrust faults are inferred from physiographic evidence and from north-striking zones of pre-intrusive brecciation.

*Intrusion.*—Igneous intrusions followed the cessation of folding and thrust faulting. Magma first intruded the rocks on the western side of the district, forming a large stock of quartz diorite locally known as the Anticona intrusive. The Potosi, San Francisco, and Gertrudis stocks, or the Morococha intrusive, as they are known collectively, are of quartz monzonite. These stocks formed to the east of the Anticona intrusive (Fig. 2). The stocks are elongated north-south and are distributed in an east-west direction.

Contact metasomatic alteration of the Potosi formation accompanied emplacement of the quartz monzonite stocks with the development of skarn and hornfels.

*Oblique Fracturing.*—Resumed compressive stress was relieved by the development of oblique fractures. These fractures form a complementary system, striking to the east, dipping steeply, and exhibiting normal and/or strike slip fault movement.

*Rock Alteration.*—Hydrothermal solutions moving through the oblique fractures thoroughly altered the rocks and deposited the sulfide ore bodies. The intrusive rocks and Catalina volcanics are silicified and sericitized. Four types of alteration are distinguished in the Potosi limestones: (1) recrystallization and dolomitization of the limestone; (2) anhydrous silicate alteration, represented by skarn and hornfels composed chiefly of diopside and tremolite

with quartz, epidote, garnet, vesuvianite and minor wollastonite; (3) hydrated silicate alteration, represented by rock composed principally of serpentine, chlorite, and talc; and (4) anhydrite alteration, a mixture of anhydrite and gypsum interlayered with marble, hornfels, and hydrated silicate minerals.

The alteration of the Potosi formation is visualized as a continuous process which started prior to igneous intrusion and continued to the close of ore

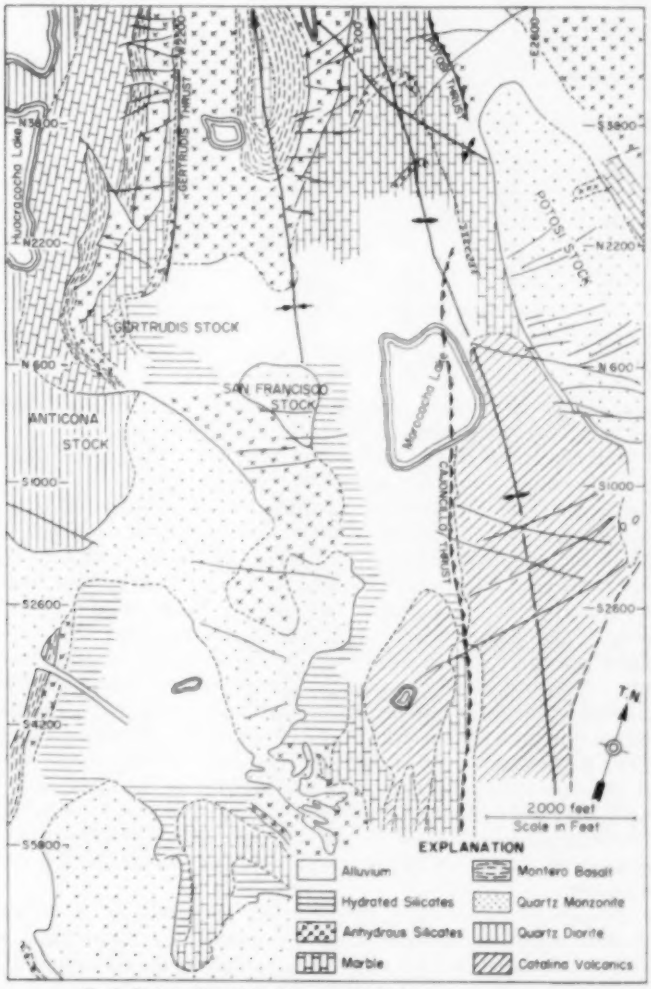


Fig 2 - Geologic Map of the Morococha District.

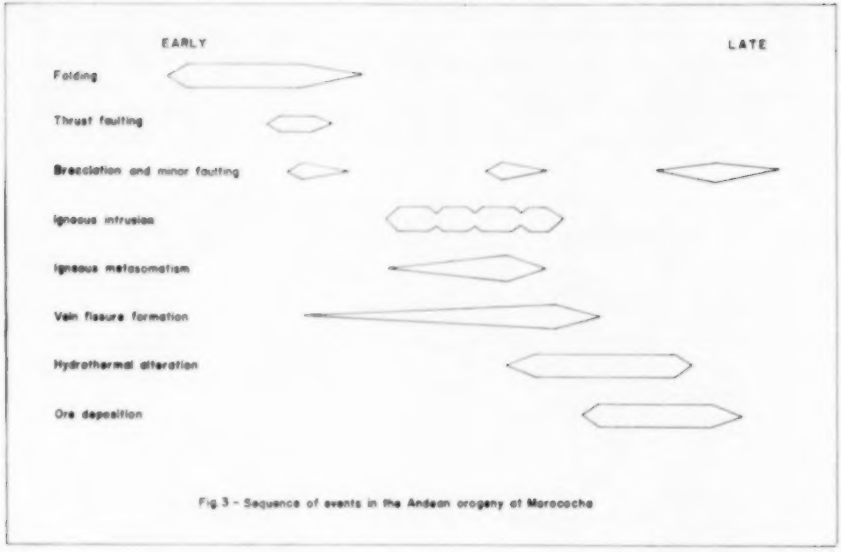


Fig 3 - Sequence of events in the Andean orogeny at Morococha

deposition (Fig. 3). Early thermal and igneous metasomatic alteration products were altered by later hydrothermal solutions.

The distribution of the alteration products is a consequence of (1) the dominant alteration processes acting in a given place, (2) the original constituents and earlier alteration products of the Potosi formation, and (3) the folded and faulted state of the Potosi formation. In general, the marble is at the periphery of the district and is interlayered with the outermost hornfelsic horizons. The hornfels is widespread, extending more than 5,000 feet from intrusive contacts, and is closer to the center of the district than the marble. The skarn and the hydrated silicate rock are near to centers of intrusive activity. Pyrite, magnetite, ludwigite, and pyrrhotite are locally abundant. The anhydrite surrounds the Gertrudis stock below the 750 level and is located between the marble on the west flank of the major anticline and the silicated and hydrated silicate rocks to the east. Modifications in this generalized pattern are present and are probably related to the dominant physical and chemical controls active in any given zone of alteration.

The physical properties of the altered rocks exerted a controlling influence on the formation of ore bodies in the district. These properties are summarized in Table 2 and are further detailed in the discussion of the oblique fracture system.

*Ore deposition.*—The major economic ore minerals of Morococha are enargite, tetrahedrite-tennantite, chalcopyrite, galena, and sphalerite. Bornite and covellite are abundant and widespread. Molybdenite is extensively distributed in small quartz veinlets in the San Francisco and Gertrudis stocks.

TABLE 2

ALTERATION PRODUCTS OF THE POTOSI FORMATION

| Alteration | Mineralogy | Physical properties | Distribution | Origin |
|---|---|---|---|---|
| Marble | Calcite, dolomite. | Competent, white to black. Host for ore minerals. | Outer margins of the district. Dolomite most abundant near ore bodies. | Recrystallization through thermal metamorphism. Dolomitization through alteration of previously developed silicate minerals. |
| Silicated Alteration (Calc-hornfels and skarn) | Diopside, tremolite epidote, garnet (grossularite), actinolite, biotite, quartz plagioclase, adularia, sulfides, wollastonite, hedenbergite, forsterite, vesuvianite, and scapolite. | Hard, brittle, white. Controls ore shoots in vein structures. | In layers corresponding to certain horizons of the Potosi formation, and adjacent to intrusive contacts. | Thermal metamorphism of arenaceous dolomitic beds of the Potosi formation, and igneous metasomatism. |
| Hydrated Silicate Alteration | Serpentine, chlorite, talc, sulfides, magnetite, ludwigite, and silica | Soft, green to white, incompetent. Contains pipe ore bodies, but few vein structures. | Between silicated alteration horizons, and adjacent to intrusive contacts. | Hydrothermal metasomatism of the silicated alteration, supplemented by action of hydrothermal ore solutions. |
| Anhydrite | Ahnydrite, gypsum, relicts of silicates, and carbonates. | Soft, plastic, tough, white, brown, translucent. Contains no ore bodies. | Below the 750 level on western flank of the major anticline. | According to Haapala: Syngenetic with the Mitu or Potosi formation.<br><br>According to Nagell: Post-intrusive and pre-ore hydrothermal alteration of the Potosi formation. |

Pyrite and magnetite are the most abundant and widely distributed metallic minerals. Pyrrhotite is locally abundant. Of minor importance are sternbergite, stephanite, aikenite, emplectite, scheelite, huebnerite, chalcocite, famatinite, cubanite, bournonite, greenockite, alabandite, hematite and arsenopyrite.

Ore bodies fall into three classifications according to their form. Vein ore bodies are tabular masses in the steeply dipping oblique fracture system. Although ore minerals are distributed throughout the vein, only those parts that widen into ore shoots are mineable. In veins less than one foot wide, mineable grade is not attained unless the ore is exceptionally rich. The near surface parts of the veins are mineable for most of their length. At depth the veins bottom in downward protuberances in small ore shoots isolated from the main ore shoots. Most of the ore shoots show a horizontal to vertical length ratio of 4 to 1. The ore minerals are mostly in open space fillings. Replacement by ores is uncommon except where fragments of the host rock are a part of the vein matter.

Pipe ore bodies are vertically elongate cylindrical masses of pyrite and copper ore minerals. Most of the pipes are associated with intrusive contacts (contact pipes) or are in discordant relation to the bedding of the Potosi formation. The ore minerals are disseminated in massive pyrite throughout the pipes, but, in places, a horizontal zonation is present where the outermost parts of the pipe are richest in ore minerals. Vertical zoning in the pipes is shown by the change from barren pyrite at the bottom through copper ore to zinc-rich copper ores near the top. The length to diameter ratio of the pipes is extremely variable and is generally in excess of 4 to 1. Open space filling and replacement textures are present in all of the pipes.

Mantos in this district are gently plunging pipe-shaped ore bodies which are accordant with the bedding of the Potosi formation. At Morococha the term "manto" has been applied to some ore bodies that are more properly classified as contact pipes. The mantos are similar to the pipe ore bodies in their elongate cylindrical shape and vertical mineralogical zoning. In general, the length to diameter ratio of the mantos is greater than that of the vein ore shoots and pipe ore bodies. Length to diameter ratios in the Churruca-Recuperada mantos are 12 to 1 and the remarkably persistent Ombla Manto has a ratio of 26 to 1. The horizontal sectional area of pipe and mantos ranges from a few hundred square feet in the smaller ore bodies to 75,000 square feet in the Ombla Manto.

Most of the pipe ore bodies and mantos grade upward into vein structures. Small tabular fin-like mantos extend from some of these vein structures. Contact pipes adjacent to the Gertrudis stock are isolated from vein structures.

### *Depth and Temperature of Ore Mineralization*

In the Morococha district, ore bodies extend upward 2,000 feet to the ground surface where the Catalina volcanics crop out. Ore mineralization in the upper horizons of the Potosi formation represents a minimum total vertical extent of ore mineralization of 3,500 feet. The Santo Toribio formation is

not ore bearing where it crops out on the fringes of the district, and no evidence remains to indicate that it was mineralized over the center of the district. If the assumption is allowed that the Santo Toribio and Machay formations were present at the time of ore deposition, then the thickness of the cover over the deepest ore bodies was 7,000 feet. The thickness of any Tertiary formations that may have been present is unknown.

To the west, in the adjacent Casapalca district (Fig. 1), the veins cut the lower members of the Tertiary Rio Blanco formation. The lowermost mine level is 3,500 feet below the outcrop. McKinstry and Noble (1932, p. 520) indicate that another 10,000 feet of the Rio Blanco formation could have lain above the present outcrop of the veins, but the depth of erosion at the time of ore deposition is unknown. The Casapalca ore deposits are classified as corresponding to the leptothermal depth-temperature zone (7).

The mineralogical composition and texture of the Morococha ore deposits are suggestive of Lindgren's mesothermal depth-temperature zone. Enargite, chalcopyrite, and tetrahedrite are the dominant ore minerals in the central part of the district. Minor quantities of molybdenite, chalcopyrite and scheelite are in disseminations and small veinlets. Quartz, sericite, ankerite and rhodochrosite are the principal gangue minerals. Sericite is widespread in the monzonite intrusives. The ratio of sulfide minerals to gangue is high in contrast to the low ratios prevailing in most epithermal deposits. Replacement textures dominate. Although many of the ore bodies have been deposited as open space fillings, the fine textures and crustified banding characteristic of the epithermal deposits are absent.

Ore bodies adjacent to the intrusives are of the same mesothermal suite of ores found throughout the district and are not pyrometasomatic replacements.

### THE OBLIQUE FRACTURE SYSTEM

The oblique fracture system is transverse to the regional trend of the folded focks. Strikes range from N 65° E to N 60° W and dips range from 65° N to 60° S. Some of the more steeply dipping fractures exhibit both north and south dips. As used here, the term "vein structures" is synonymous with the term "oblique fractures." These fractures are faults of small displacements and apparently fall into two systems. Each system comprises two sets. The northeast and northwest striking sets form one system, and the south and north dipping sets form the other system. The two fault systems locally share a given fracture; i.e., a particular fracture may exhibit characteristics of both systems by variations of dip and strike.

All rock types are cut by the oblique fractures except the anhydrite and the lower part of the Gertrudis stock.

The most continuous individual fractures are in the Catalina volcanics and the San Francisco stock. Here, the Cecilia Vein and the Manuelita Vein are each 3,200 feet long. A continuous fracture 5,800 feet long extending from the eastern contact of the Catalina volcanics to the western contact of the San Francisco stock includes the La Paz 146 Vein and the San Francisco Vein 4. Veins in the Potosi formation are mostly less than 1,000 feet long.

A notable exception is the Cobriza Vein 9, which cuts through the marble and silicated rocks for 2,000 feet.

The width of the vein structures ranges from less than an inch to 20 feet. The widest parts are related to dilation that accompanied normal fault movement. Most of the ore bodies in the oblique fractures are about 3 feet wide.

Most of the oblique fractures are post-intrusive. The Potosi formation and Catalina volcanics contain both northeast and northwest striking fractures in equal abundance. A pre-intrusive age for some of the northwest striking fractures is indicated by northwest striking monzonite dikes and the relative paucity of this set in the Morococha intrusives. The fractures formed over a span of time, as shown by vaulted veins. A post-ore age of fracturing may be indicated by unmineralized fractures and post-ore brecciation.

Splits are narrow short fractures branching from the major oblique fractures. The larger splits are where the major oblique fractures change strike and the splits continue along the original strike direction. Where the major vein structures are closely spaced, small connecting splits are present. The smallest splits are minor fractures of various attitudes bounding the major vein structure. Splits rarely cross the major vein structures.

*Displacement.*—The absolute displacement can be accurately determined on few of the oblique fractures for rarely is a set of reference points found in both vein walls. Slickensides are generally present in the gouge and, in many places, several directions of movement are indicated. Apparent horizontal displacement, slickenside orientation, and the horizontal intersection of vein structures and tension fractures indicate normal fault movement on most vein structures. Some of the displaced contact-vein relationships cannot be explained by normal fault movement and it is concluded that reverse or strike slip movement is present. No tension fractures clearly indicating such movement were seen by the writer.

Attempts to match minor fractures on opposite walls of the vein structure were unsuccessful and it is concluded that minor splits and fractures are not represented in both walls of the vein structures.

Faulting of vein ore bodies is not a serious problem at Morococha. Only three such cases are known, and the displacement does not exceed 25 feet. Normal fault movement on San Francisco Vein 1 has displaced San Francisco Vein 2 twenty feet (Fig. 4). Most of the slickensides in the gouge in San Francisco Vein 1 plunge down dip indicating a dip slip component of motion. These two vein structures are nearly parallel and the intersection plunges 10° west. The segment of San Francisco Vein 1 between the offset parts of San Francisco Vein 2 is barren; the ore mineralization is coherent and unshattered as it wraps from one structure to the other. This suggests that the displacement is of pre-ore age. Ore solutions, ascending on the two veins, were diverted at the junctions of the two veins by the impermeable gouge zone between the offset parts of San Francisco Vein 2.

The Cecilia Vein strikes to the east and dips 70° north. A fault striking N 20° E and dipping 70° east displaces the eastern segment of the vein 22 feet to the south (relative to the western segment). This fault is known over

a vertical distance of more than 700 feet. Slickensides in the fault gouge are strongly developed but randomly oriented so that the direction of absolute movement cannot be determined. As no drag ore is present in the fault, the relative age of the fault is not clear.

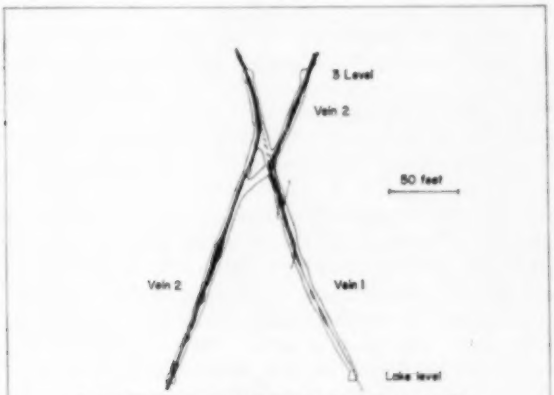


Fig. 4 – Vertical section, looking east, San Francisco Vein 2 offset by San Francisco Vein 1.

Fig. 5 – Plan, 3 level, Rectificadora 56 Vein displaced by fault.

The Rectificadora 56 Vein, striking N 60° E and dipping 65° north, is offset by a fault striking N 50° W and dipping 70° southwest. The western segment of the vein is displaced 25 feet to the southeast relative to the eastern segment of the vein (Fig. 5). Near the fault, the vein increases in width, and a heavy dissemination of pyrite extends from the vein along the fault. Sulfide minerals along the fault are not crushed or fractured. The fault is considered to be of pre-ore age. Consideration of a theoretical left lateral movement or the customary normal fault movement indicated that the western

segment of the vein should lie to the south. Subsequent exploration proved this to be true.

*Wall Rock Control.*—The physical properties of the various rock types in the Morococha district have exerted control on the development of the oblique fractures. The rocks may be ranked in order of decreasing ability to support well defined continuous fractures, as follows: Catalina volcanics, Morococha and Anticona intrusives, anhydrous silicate rock, marble, hydrated silicate rock, and anhydrite. Strong, well defined vein structures in the competent Catalina volcanics and San Francisco stock split into minor subsidiary fractures and disappear at contacts with the hydrated silicate rock. Only the strongest fractures persist in the hydrated silicate rock and none are present in the anhydrite. Continuity along the strike and dip of the fracture is greatest in the harder, less plastic rocks.

*Theoretical Considerations.*—The major agent of deformation in the Morococha district is horizontally directed east-west compression. This is readily deduced from the regional north-trending folds and the early development of north-striking thrust faults. In addition to a system of complementary thrust faults, a complementary strike-slip fault system may be expected to form under this stress system. The development of normal faults requires a theoretical rotation of the major stress axes to a vertical position. As normal faults are much more evident than strike-slip faults in the Morococha district, an explanation consistent with theory is required. The explanation for this apparent anomaly lies in the deviation from ideal conditions of stress and rupture at Morococha. These conditions are, (1) anisotropy of the rocks, i.e., the physical properties of the rocks vary within the district, (2) more than one period of fracturing has occurred, and (3) plastic deformation has preceded fracturing. The effect of varying physical properties of the rocks (plasticity) is related to the angle of internal friction (5, p. 365). This angle is larger in brittle rocks than in plastic rocks. Fractures in brittle rocks form at more acute angles to the axis of maximum stress than in plastic rocks. This is illustrated by the greater range in attitude exhibited by faults in the Potosi formation as compared to those in the Catalina volcanics and is related to variations in the angle of internal friction within the various sedimentary beds.

Movement on an early set of fractures may relieve later stresses even if the fractures do not bear precise relation to stress required by theory. Mathematical treatment of the effect of faulting on the direction and intensity of stress distribution (1, pp. 160 to 173) shows that preexisting faults tend to diminish the stress near the center of the fault and to inhibit the development of more faults in the vicinity. Anderson (1, p. 187) described normal faults in the Scottish Carboniferous which range in dip from 67½ to 72 degrees. A dip of 63 degrees is quoted by Hubbert (5, p. 358) as most common among normal faults in a coal field in Holland. The normal faults in the Morococha district have an average dip of 73 degrees, which is more closely related to the steep dips of strike-slip faults. This suggests that fractures in the district originated as strike-dip faults, but that most of the later movement was in the direction of the dip.

Elongation of the district in a north-south direction in response to east-west compression provides a clue to the origin of the normal faults. Billings (2, p. 358) in describing the elongation of conglomerate pebbles parallel to the fold axes of Carboniferous sediments near Newport, Rhode Island, stated, "Under east-west compression the sediments were thrown into folds striking north-south, and thus the sediments elongated in that direction." Although no linear elements indicating north-south elongation have been noted at Morococha, the development of normal faults (extension faults) indicates elongation in this direction.

Anderson (1, p. 15) related the formation of normal faults to relief of pressure in all horizontal directions. As normal faulting is the most recent manifestation of faulting at Morococha, it may be correlated with relaxation of stress generated by the Andean orogeny.

The development of the structural geology of the Morococha district during the Andean orogeny followed an orderly pattern. Folding and thrust faulting in response to east-west compression were followed by igneous intrusion and rock alteration. The oblique fractures developed as a result of continued compressive stress and did not reach their maximum development until the relaxation of this stress.

With well ordered timing, hydrothermal ore fluids followed the completion of the ground preparation. The oblique fracture systems and igneous contacts provided channels for the ascent and distribution of the ore fluids.

## ORE CONTROLS

For convenience in the discussion of ore controls, the district is divided into the western and eastern parts. Vein structures are the chief ore body types in the eastern part of the district and pipe and manto ore bodies are most abundant in the western part of the district. The two parts of the district are divided at the western contact of the San Francisco stock at coordinate W2200 (Fig. 2).

### *Eastern Morococha District*

The geology of the eastern part of the district is shown on Figure 2. The Catalina volcanics and the San Francisco stock are the principal rock types. At depth, the volcanic sequence is dominant because of its anticlinal structure and northerly plunge. Ore controls pertain to vein ore bodies in and near these brittle rocks.

The veins are open space fillings of enargite, tetrahedrite, chalcopyrite, galena, sphalerite, pyrite, quartz, and barite. These minerals exhibit well developed crystals growing into open spaces. The ore mineral break cleanly from sharply defined vein walls. Replacement of the wall rock is at a minimum, especially in the Catalina volcanics; fragments of wall rock in the vein matter show partial replacement. Layers of gouge are parallel to the vein walls and are narrow with respect to the total vein width. As shown in the discussion of oblique fractures, normal fault movement is most commonly present.

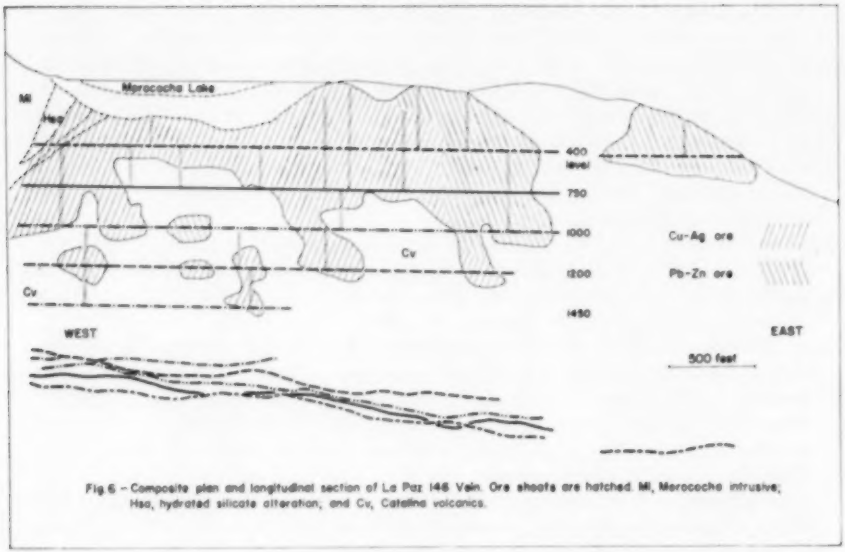


Fig. 6 – Composite plan and longitudinal section of La Paz 146 Vein. Ore shoots are hatched. MI, Morococha intrusive; Hso, hydrated silicate alteration, and Cv, Catalina volcanics.

*Dilational Control.*—Control by dilation of the wall rock is demonstrated where mineralized vein structures widen to mineable widths. In most of the veins, the ore to waste ratio is relatively constant and mineability is determined by the amount of ore extractable from a minimum practical mining width.

Veins are widest where they dip most steeply. On the deeper mine levels, where ore shoots are interspersed with waste, the dilational control is most apparent. Figures 6 and 7 are of the La Paz 146 Vein and the La Joven 26 Vein, both in the Catalina volcanics. The relation of ore shoots to the more steeply dipping parts of these veins may be seen by inspection of the composite level plans accompanying the longitudinal sections. Dilational control of ore shoots through normal fault movement is indicated.

The detection of a dilational control of the ore shoots aids in predicting the location of new ore shoots. Levels in the Morococha mine are about 200 feet apart. In the past, vein structures were not always tested by vertical exploration above barren parts of the drifts, even where small ore showings were exposed. In recent years, unsuspected ore between the levels has been found by raising in these old drifts. Where ore showings can be related to dilational control, the continuity of the ore is more readily estimated.

In places, the dilation control of ore shoots is too subtle for recognition by inspection of composite level plans and sections. In such cases, contouring of the vein surface (3) or the preparation of dilation diagrams from contoured vein surfaces (10) may aid in prospecting. In those parts of vein structures close to the contacts of the Catalina volcanics and the San Francisco stock,

contact control of ore shoots overshadows the dilational control of wall rock movement.

*Contact Control.*—One of the most effective controls on the localization of ore shoots in the district is contact control. Ore shoots favor the brittle rock of the Catalina volcanics, Morococha intrusive, and silicated alteration over the soft incompetent hydrated silicate alteration. Figures 7 and 8 illustrate the localization of ore in the San Francisco Vein 6 and La Joven 26 Vein at the San Francisco stock and Catalina volcanics contacts. These veins are traceable only as irregular pyritized slips in the adjacent hydrated silicate alteration.

Contact ore control is related to the channels of ascent of the ore fluids. Ore fluids ascending along the contacts of the San Francisco stock and the Catalina volcanics entered the zone of fracturing and found ingress to

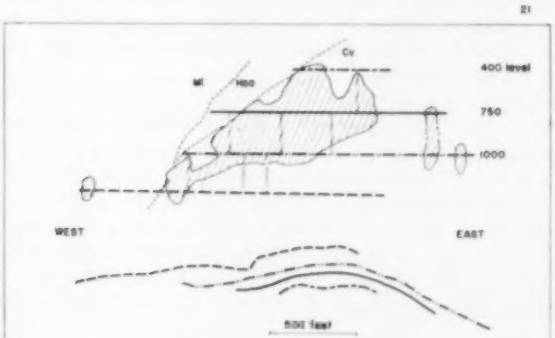


Fig. 7—Composite plan and section of La Joven 26 Vein. Ore shoots are crosshatched. Mi, Morococha intrusive; Hsa, hydrated silicate alteration; Cv, Catalina volcanics.

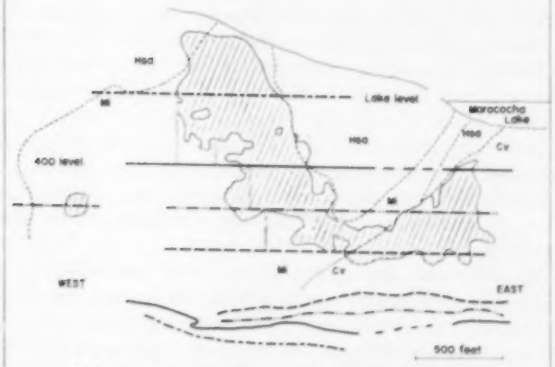


Fig. 8—Composite plan and section of San Francisco Vein 6. Ore shoots are crosshatched. Mi, Morococha intrusive; Hsa, hydrated silicate alteration; Cv, Catalina volcanics.

the brittle rock mass through the oblique fractures. The ore fluids were guided into the oblique fractures by the damming effect of the relatively unfractured hydrated silicate rocks in contact with the stock and the volcanics. Chlorite, as a gangue mineral in the veins, is found only close to the contacts. Furthermore, the decrease in intensity of ore mineralization toward the interior of the San Francisco stock and the Catalina volcanics is regarded as evidence against the ascent of ore fluids within these rocks. Neither the San Francisco stock nor the other Morococha intrusives were the source of the ore fluids.

The obvious application of contact control to prospecting is to drive crosscuts within the intrusives and volcanics as close as possible to the contact.

*Zoning Control.*—Zoning in the distribution of the ore minerals may be present in a single ore body. The La Paz 146 Vein (Fig. 6) shows the change from copper ores to lead and zinc ores toward the eastern end of the vein. Galena and sphalerite increase at the expense of chalcopyrite and tetrahedrite. Vertical zoning is shown where lead-zinc ore overlies copper ore near the center of the vein.

The Yankee Vein 2 and Pipe ore body is a striking example of vertical zonation. From the 1,200 level up to the 1,000 level, the copper ore is in a vein and is localized at the Catalina volcanics contact. The minerals are chalcopyrite, tetrahedrite and bornite. Upward toward the 750 level, pyritic silicified hydrated silicate rock is present. The vein is less sharply defined and merges into a pyritic copper-bearing pipe ore body. The pipe persists up to the 222 level, but above the 400 level, a lead-zinc bearing vein structure is the major part of the ore body. The galena and sphalerite in the vein structure show a vertical and lateral relationship to the central copper-bearing pipe.

The zoning control on ore mineralization supports the view that the ore fluids were guided upward along restricted channelways into the zone of fracturing. Here they spread out into the oblique fracture system.

Prospecting is necessarily guided by the type of ore desired. In the outer extremities of vein structures and at the periphery of the district lead-zinc ores are found. Conversely, the centers of ore mineralization provide copper ores, and their location is indicated by the mineralogical changes in the ore body.

*Vein Intersection Control.*—The extent to which vein intersections localize ore bodies varies with the wall rock. In the western part of the district, pipes and mantos show a definite relation to intersecting fractures. In the eastern part of the district, in the Morococha intrusives and Catalina volcanics, no consistent localization of ore shoots is noted.

Few of the major vein structures join or cross one another. Most of the vein intersections are where splits branch from the main vein structure. Some of the splits are barren, some are ore bearing away from the junction, some are ore bearing at the junction, and some of the splits assume the characteristics of the main vein structure, which in turn pinches out like a split. Fracturing of the wedge of rock in the acute angle of the vein junction is not extensive. A notable exception is the previously described fault junction

between the San Francisco Vein 1 and San Francisco Vein 2 (Fig. 4). Here, the narrow San Francisco Vein 1 expands at the vein junction to an ore body 10 feet wide.

*Depth Control.*—Most of the vein ore bodies are barren below the 1,200 level. The uppermost parts of the veins carry continuous ore mineralization independent of structural control except for contact control. The hydrated silicate alteration is a definite limiting factor on vein ore bodies throughout the Morococha district. At depth, ore shoots in the veins bottom with no apparent change in wall rock or vein attitude. Where veins are in excess of 3 feet in width near the surface, at depth they are mere cracks mineralized with quartz and pyrite. Below the 750 mine level there is a marked decrease in the total number and strength of the vein structures.

A few of the ore bodies bottom at relatively shallow depth (e.g., the Rectificadora 131 Vein) with no decrease in width. The structure is strong, a full 3 feet in width, but carries only barren quartz and pyrite below the overlying chalcopyrite and tetrahedrite ore shoots.

Depth control on ore mineralization in the Morococha district is primarily the result of a lack of suitable vein structures at depth. Clogging of parts of a vein structure by barren quartz and pyrite may have hindered ore mineralization in some of the veins, but this is a minor factor. Another factor, the effectiveness of which is not fully evaluated, is that of physical-chemical controls on the precipitation of ore minerals from the ore fluid.

Pipe and manto ore bodies persist to greater depths in the western part of the district than do the vein structures.

### *Western Morococha District*

In the western part of the district, the major rock types are alteration products of the Potosi formation and the Gertrudis stock. The softer, more plastic lithology of the western part of the district, as compared to the brittle lithology of the eastern part of the district, is accompanied by a change in the ore body types. Veins, although abundant in the silicated alteration and marble of the Potosi formation, are subordinate in economic importance to pipe and manto ore bodies.

Open space-filling textures, such as vugs lined with crystals of sulfide minerals, are abundantly distributed. However, replacement of the Potosi formation by massive sulfides is the major process of ore emplacement. Partly replaced layers of gouge and beds of the Potosi formation are sporadically preserved in the massive sulfide pipes and mantos.

Contact controls of ore localization include contacts between alteration layers of the Potosi formation and contacts between intrusives and the Potosi formation. Intersections of fractures with limestone alteration contacts, with igneous contacts, and with other fractures are an additional controlling influence for the localization of pipe and manto ore bodies. Pre-ore breccias are a host for some of the mantos. Post-ore brecciation has displaced and scattered some of the ore bodies.

*Limestone Alteration Control.*—Ore shoots in veins in the silicated

alteration layers of the Potosi formation rake to the west in accordance with the westerly dip of the bedding. The marble supports well defined vein structures in the upper mine levels, but it is not a consistently productive horizon at depth. The vein minerals fill open spaces in the marble; replacement is at a minimum. As in the eastern part of the district, the hydrated silicate rock is an unfavorable host for vein ore bodies. The anhydrite alteration is devoid of vein structures.

Manto ore bodies are localized at contacts of the silicated rock with marble, and with hydrated silicate rock. This is illustrated by the Toro Mocho 265 Vein and Dante Manto. The Dante Manto is in a silicated horizon at the hanging wall contact with hydrated silicate rock and plunges to the west in accordance with the steeply dipping contact. The Toro Mocho 265 Vein, leading from the Dante Manto, is found only in the silicated rock. Weak chalcopyrite and sphalerite ore in the vein merge into the rich enargite and tetrahedrite ore of the manto. Below the 222 level, the ore grades downward into massive barren pyrite. This ore body is unusual because enargite is rarely found in quantity far removed from igneous masses in the Morococha district.

*Intrusive Contact Control.*—Vertical chimney-shaped ore pipes are at the western contact of the San Francisco stock. These ore pipes are in hydrated silicate rock at, or within 150 feet of the stock contact. One or more vein structures extend from the pipes into the stock. Ore shoots in these veins are within the stock. Above the 750 level, the chalcopyrite and tetrahedrite are the chief ore minerals. Below the 750 level, the ore disappears in pyritic brecciated hydrated silicate rock.

The most striking example of intrusive contact control is provided by the contact ore pipes associated with the Gertrudis stock. These ore bodies are in the form of discontinuous tabular ribbons up to 15 feet thick, which twine around the stock adhering strictly to the contacts. Most of the pipes are massive ore bodies of enargite, tennantite-tetrahedrite, and pyrite. A small amount of chalcopyrite and sphalerite is in the uppermost parts of the pipes. In places, the ore minerals are in heavy dissemination at the stock contact. Short, narrow cracks in the wall rock contain ore minerals, but no vein structures are present. In general, the ores are not vuggy, but, open space-filling textures are shown by beautifully terminated crystals of enargite and tetrahedrite.

Above the 400 level, the pipe ore bodies grade upward into vein structures. Below the 750 level, anhydrite surrounds the Gertrudis stock and San Nicolas plug. The anhydrite in contact with the ore is coarsely crystalline and pink; in contact with the Gertrudis stock, it is medium grained and dull white.

As no vein structures are present in either the anhydrite or the Gertrudis stock, the contact itself was the only channelway of ascent for the ore solutions. The origin of these channelways is suggested by their position on hanging wall contacts of the stock. Two possibilities of origin are considered: (1) the stock contracted as it cooled and settled toward the footwall leaving open spaces along the hanging wall, and (2) the ascending ore solutions were capable of dissolving their own channelways in the anhydrite.

Data presented by Hulin (6, p. 51) on the coefficient of linear expansion of granite is as follows:

| | | |
|---|---|---|
| Temperature range | 20° to 300° C | $13.2\ 10^{-6}$ |
| | 150° to 300° C | $18.0\ 10^{-6}$ |
| | 300° to 600° C | $43.5\ 10^{-6}$ |

If the Gertrudis stock began to crystallize at 700° C and cooled to 300° C prior to ore mineralization, the linear contraction would be 0.43 feet per 100 feet for every 100° C temperature drop. On the 1,000 level, the stock is 600 feet in diameter and should contract 10.32 feet through a temperature drop of 400° C. An additional 1.62 feet of contraction would take place in cooling from 300 to 150° C, a reasonable temperature at which ore mineralization may have ceased. The width of the pipes range from a thin film to 15 feet with most of them less than 10 feet in width. This agrees with the calculated width of open spaces formed by contraction cooling. A possible objection to this theory is in the timing of the anhydritization of the Potosi formation. Evidence has been presented (9) showing that the anhydrite is younger than the Gertrudis stock. Anhydrite in contact with an intrusive mass at temperatures up to 700° C would expectably show evidence of recrystallization at the stock contacts. Recrystallization of the anhydrite is seen only in contact with the ore pipes.

The second possibility, that the ore solutions were capable of dissolving their own channelways, does not explain the preference of ore bodies for the hanging wall intrusive contacts over random distribution within the anhydrite complex. Any open space available at igneous contacts, however, would provide the most logical path of ascent for ore solutions trapped under the structureless anhydrite. Such an open space may have been provided by a small amount of contraction of the Gertrudis stock in the lower temperature ranges following anhydritization. The later ascending ore solutions were able to enlarge these open spaces through solution of the anhydrite.

The western side of the San Francisco stock has been thoroughly developed. The vein structures within the stock guided exploration to the pipe ore bodies early in the history of the district.

Prospecting along the contacts of the Gertrudis stock located the Gertrudis contact pipes. Unfortunately, these ore pipes have no vein structures to guide prospecting. In recent years, diamond drill holes directed at hanging wall contacts of the stock have been successful in finding new ore below the 1,000 level.

*Fracture Intersection Control.*—Control by fractures on the localization of pipe and manto ore bodies fall into three groupings: (1) intersections of veins in igneous contacts, (2) intersections of veins and altered limestone contacts, and (3) intersections of veins with other fractures.

The association of veins with contact pipes and mantos localized at contacts has been described above. Although the primary control on these ore bodies is the contact, fault movement transverse to the contact promoted brecciation or zones of weakness susceptible to permeation by the ore solutions. These

zones of weakness extend to the lowest level of mine development and have provided channelways for the ascending ore solutions.

The localization of pipes and mantos has been effected by intersecting fractures as illustrated by the Ombla Manto (Fig. 9). The part of the manto above the 400 level is a network of veins and is here referred to as

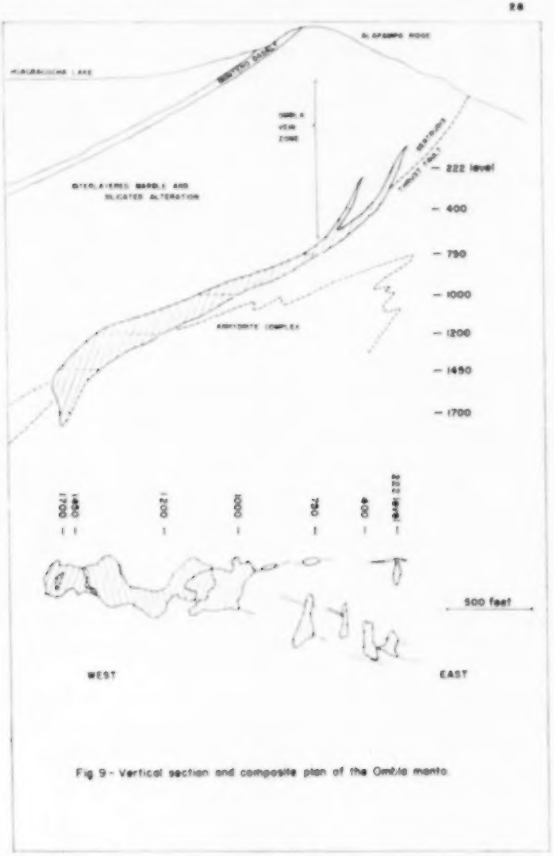


Fig 9 - Vertical section and composite plan of the Ombla manto

the Ombla vein zone. With increasing depth, the vein structures become subordinate to the gently west plunging cylindrical mass of sulfides. Below the 1,200 level, vein structures persist only as small barren fractures in the wall rock. The plunge of the manto conforms to the west dipping Potosi formation and coincides with the downward projection of the Gertrudis thrust fault.

Small subsidiary mantos in the Ombla vein zone are elongate in a north-south direction. As they are related to limestone alteration contacts, stratigraphic control or control by the Gertrudis thrust fault is indicated. The deeper parts of the manto (Fig. 9) are equidimensional or are elongate in an east-west direction and are not related to stratigraphic control.

The manto is zoned horizontally. At the core is massive to coarsely crystalline pyrite. Cubes and pyritohedrons up to 6 inches in diameter are in the vuggy parts accompanied by well formed quartz crystals. Copper assays less than 0.4 percent in the pyritic core, although, in places, an ill defined zone of chalcopyrite penetrates into the core of pyrite. Chalcopyrite is the most abundant ore mineral and is closest to the pyritic core. Tetrahedrite, bornite, covellite, sphalerite, and galena are common and are on the wall rock side of the chalcopyrite. The copper minerals are most abundant on the steep side walls of the manto. Sphalerite and galena, where present, are on the outermost contact of the manto. Sphalerite is most abundant on the footwall of the manto.

The upper part of the manto is especially vuggy and shows evidence of open space filling. At depth, replacement textures dominate. Remnants of the Potosi formation are present as small, partly replaced silicified lenses. Discontinuous layers of gouge, which may represent pre-ore fractures, have also resisted replacement.

Sharply angular fragments of anhydrite and marble at the contacts of the manto are the result of collapse brecciation related to solution of the wall rock along water courses in the manto. The water courses persist down to the 1,450 level.

The origin of the manto is through massive sulfide replacement of the Potosi formation.The control of the localization of the manto is through shattering of the Potosi formation in the space now occupied by the manto. W. C. Lacy (personal communication, 1955) suggested that the manto may represent a breccia pipe formed through sudden upward stress from an intrusive below the 1,700 level. This is difficult to reconcile with the restriction of the manto to a well defined pipe having a length to diameter ratio of 26 to 1 and an inclination of 30 degrees. Also, no increase in the intensity of the limestone alteration is detectable on the 1,700 level which would indicate the proximity of an intrusive mass at depth.

The concentration of vein structures intersecting in proximity to the Gertrudis thrust fault cannot be ignored. Recurrent movement on the thrust fault and the Ombla vein structures would produce a shattered zone of rock in the present form and position of the Ombla Manto.

*Breccia Control.*—In addition to local breccias at contacts and vein intersections, large pre-intrusive breccias have also provided a host for ore bodies. An example is provided by the Churruca-Recuperada Mantos on the hanging wall of the Montero basalt in the Churruca breccia. Here, the ore minerals bornite, tetrahedrite, and pyrite are shattered, but are not as extensively brecciated as the limestone host rock.

In addition to providing a host for the ore bodies, the breccias limit their

extent. Post-ore collapse breccias in contact with ore have scattered parts of the ore bodies and diluted them with waste. The Toro Mocho Contact Pipes, among others, illustrates the case. The rich enargite-tetrahedrite bearing pipes were mined down to the 750 level. Below the 750 level, widespread brecciation of the anhydrite complex, marble, and quartz monzonite underlies the pipes and dilutes the ore with waste. The Riqueza 100 Ore Body also bottomed in breccias which scattered and diluted the ore.

The age of these breccias is clearly post-ore and their origin is the result of solution of the anhydrite complex by meteoric waters (9).

## ORE FLUID CHANNELWAYS

The centers of ore mineralization are in the San Francisco, Toro Mocho, Gertrudis, Ombla, and Central mine blocks. The manto and pipe ore bodies are distributed from the Ombla Manto S 80° E through the Amistad Pipe, Yankee Vein 2 and Pipe, to the Riqueza 100 Ore Body for a distance of 3,800 feet. From the Ombla Manto to the south are the Gertrudis contact pipes, Dante Manto, and San Miguel Manto. These east and south trending lines of mantos intersect at the Ombla Manto. The north-south line corresponds in position to the southerly projection of the Gertrudis thrust fault and the east-west lines (S 80° E) corresponds to the easterly projection of the Ombla vein zone. In addition to the deep rooted ore bodies along these lines, are the ore bodies associated with the contacts of the San Francisco stock and the adjacent western contact of the Catalina volcanics. These pipe ore bodies and the stock contacts have served as conduits for ore solutions rising from depth. Away from these conduits, to the west, south, and east, ore is contained in vein structures and bottoms at increasingly higher levels.

Vein structures associated with the pipe and manto ore bodies have been regarded as "feeders" to these ore bodies. McLaughlin, Graton, and others (8, p. 536) stated, "Invariably a vein or a fracture appears to have acted as a feeder for the manto(s)." This idea is also expressed by the Geological Staff (4, p. 173). "The mantos are fed by veins, or more rarely by pipes, that cross the horizon susceptible to replacement; but occasionally an ore body of manto-like attitude is localized by the highly fractured condition of the containing horizon rather than by its favorable chemical character." The pipes are here considered as the conduits that guided the ore to the veins. Empirical evidence for this is as follows: (1) Vein structures are only weakly developed or are absent at the lower levels of pipe and manto ore bodies. Where vein structures are absent, it would be necessary to assume downward circulating ore solutions if the veins are regarded as the primary ore channels. (2) Ore within the veins is most closely associated with the pipes and mantos. (3) Replacement of the vein walls by the ore minerals is negligible in contrast to the extensive wall rock replacement in the pipes. This indicates that the intensity of the ore solutions declined away from the pipes. (4) Mineralogical zoning relationships, as in Yankee Vein 2 and Pipe, also suggests that the ore solutions migrated outward from central pipe-like conduits.

SUMMARY OF PROSPECTING GUIDES

In the preceding sections, the writer has endeavored to trace the orogenic history of the Morococha district and to show the relationship between the localization of ore deposits and structural features. The following is a summary of the effects of folding, thrust faulting, brecciation, igneous intrusion, rock alteration, and oblique faulting on ore localization. An understanding of the geological controls on ore deposition provides a guide for continued prospecting in the district.

*Folding.*—The anticlinorium of the Morococha district is regarded as a primary but indirect control on the ore mineralization. The distribution of the alteration horizons of the Potosi formation is the result of the early established fold pattern. Where the folds yielded to increasing compressive stress, thrust faults developed which provided zones of weakness and channels of ascent for the later ore fluids. The elongation of the intrusives in a north-south direction and their position at or near the crest of the anticlinorium represents a direct control by folding.

*Thrust Faulting.*—Although the thrust faults are not hosts to vein ore bodies, they formed zones of weakness, which localized pipe and manto ore bodies at intersections with the oblique fractures. The Gertrudis thrust fault exerted a strong controlling influence on the pipe and manto ore bodies to the south of the Ombla Manto. The district north of the line connecting the Ombla Manto and the Riqueza 100 Ore Body is relatively undeveloped. Here, lead-zinc-silver ores are exposed in shallow mine workings, but no deep level prospecting, based on structural ore controls, has been done.

*Brecciation.*—The extent to which pre-intrusive breccias controlled the localization of intrusives is obscured by post-intrusive and post-ore brecciation. Breccia control is indicated where a thick dike-like mass of quartz monzonite is adjacent to the western contact of the Catalina volcanics. Breccias provided a host for ore bodies (e.g., the Central 153 Ore Body and the Churruca-Recuperada Mantos).

Post-ore collapse breccias, associated with the anhydrite complex, scattered and diluted ore bodies in contact with them. As these breccias are of limited vertical extent, the lower extensions of some of the ore bodies may be found by prospecting beneath them.

*Intrusion.*—Igneous intrusives played a direct role in the localization of ore bodies. The intrusive contacts furnished channels for the ascending ore solutions and are hosts for contact pipe ore bodies, especially where they are intersected by the oblique fractures. Ore within the intrusives is in veins and is largely restricted to the vicinity of the contacts.

The intrusives also played an indirect role in the localization of ore bodies through thermal and metasomatic alteration of the host rock. Thermal gradients established by the intrusives persisted through ore deposition and exerted a strong influence on the mineralogical zoning in the ore deposits.

*Rock Alteration.*—Changes in the physical properties of the rocks wrought by metamorphic processes exerted a direct control on the localization of ore bodies. Silicification of the Catalina volcanics and Morococha intrusives and

silication of the Potosi formation produced brittle rocks supporting well defined vein structures. Hydrothermal alteration of the silicated alteration and anhydritization yielded soft plastic rocks incapable of supporting strong vein structures. These physical properties determined the attitude as well as the strength of the vein structures.

The distribution of these altered rocks controlled the locus of ore deposition. Contacts between the various types of altered rocks, especially where intersected by vein structures, provided zones of weakness amenable to replacement by the ore fluids. Prospecting by means of projected alteration contacts and vein intersections may find more ore in the western part of the district.

*Oblique Fracturing.*—The oblique fractures are the hosts for the vein ore bodies. The extent of these fractures is regulated by depth in the mine and by horizontal lithologic variations of the district. The intersections of these fractures with igneous contacts, limestone alteration contacts, and the Gertrudis thrust fault provided direct structural control on the location of pipe and manto ore bodies.

Utilization of these guides to structural ore control aids in the designing and evaluation of prospecting programs. Although even the most ideal combination of geological conditions does not insure the presence of ore, the recognition of these conditions provides the most effective guides to ore.

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INDUSTRIA E COMERCIO DE MINERIOS—ICOMI,
CAIXA POSTAL 396,
BELÉM, PARÁ, BRASIL,
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# ORE DEPOSITS AND SEDIMENTARY FEATURES JEFFERSON CITY MINE, TENNESSEE

DAVID L. KENDALL[1]

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ABSTRACT

The Mascot-Jefferson City zinc district, extending from about 15 to 30 miles northeast of Knoxville, lies in central East Tennessee, in the Appalachian Valley and Ridge province. The ore bodies, restricted to about 150 feet of dolomitized limestone in the Lower Ordovician Kingsport and Longview formations are elongated and continuous with bedding but are irregular in detail. Distinction is made between coarse-grained and fine-grained dolomites. Both types are believed to have been formed penecontemporaneous with deposition. Ore has been deposited as replacements and open-space fillings in coarse dolomite, but only as fracture filling in fine dolomite.

Sedimentary breccias of two principle types are distinguished: coarse-grained dolomite breccia located in dolomitized limestone beds and restricted to these beds; and, fine-grained dolomite breccias cross-cutting the stratigraphic section. Reefs of coarse dolomite, possibly of algal origin, surrounded by limestone characteristically are capped with sphalerite and are good ore guides, grading into large shoots of replacement-type ore.

Vug-filling laminated clastic dolomite with laminations parallel to country rock bedding is post-ore and indicates ore deposition while beds were flat. This, together with the marked stratigraphic restriction of the ore and its intimate association with sedimentary structures, permits an alternative to the customarily cited tectonic structure-hydrothermal theory of origin. Concentration and deposition from the sea contemporaneous with sedimentation is suggested. Later regeneration of such a deposit would explain the migration of mineralization into fractured fine-grained dolomite.

[1] Resident Geologist, The New Jersey Zinc Company, Jefferson City, Tennessee.

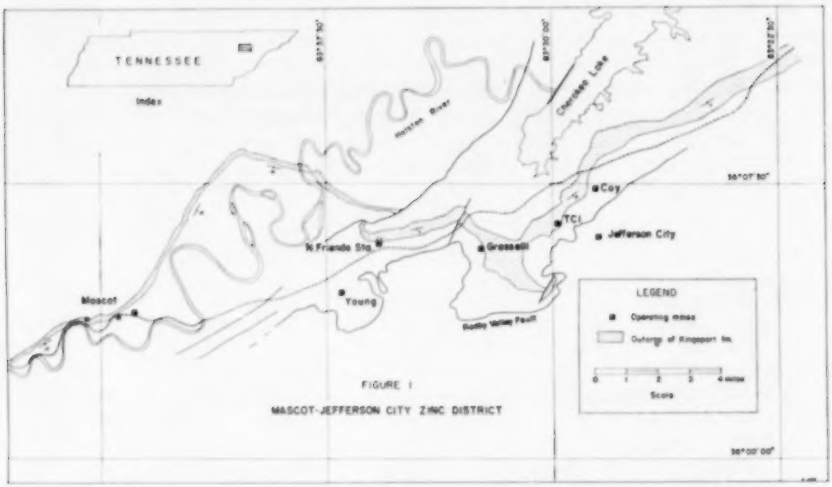


FIGURE 1
MASCOT-JEFFERSON CITY ZINC DISTRICT

## INTRODUCTION

THE Jefferson City mine is located in the northeastern part of the Mascot-Jefferson City zinc district (Fig. 1), about 30 miles from Knoxville. Development of the mine by The New Jersey Zinc Company was begun in 1953 and production commenced in 1956. The mine is now the largest single producer of zinc concentrates in the district.

Theories of the origin and depositional control of the Jefferson City-Mascot ores have ranged widely, reflecting the changing ideas in geological science. Among the early writings is that of Purdue (13) in which he points out the narrow stratigraphic limits of the ore, and the lack of igneous rocks in the vicinity of the ore deposits. Purdue speculates (13, p. 15) that as other formations in the area are structurally as favorable as the Knox but are not known to contain zinc, "it therefore seems probable that the zinc was deposited with the Knox dolomite and at rather definite horizons in that formation."

Secrist (14, p. 158) elaborated on the origin of the ores, theorizing that the minerals were derived from igneous rocks of "Appalachia" by ordinary weathering processes and deposited in the accumulating Knox sediments in finely disseminated form. Ore bodies were then formed by leaching of this disseminated mineralization by circulating ground water, and precipitation in favorable locations.

The occurrence of zinc ores in brecciated rock was noted in the earliest reports but whereas Purdue (13, p. 16) interpreted the breccias as the result of compression during orogeny, Ulrich (15) interpreted the breccias as cave or sink-hole breccias. He restated the opinion that the ore bodies were restricted stratigraphically and pointed out that cave breccias were common at this horizon, particularly overlying the principal ore bodies, implying that these breccias were the important ore localizers.

With the general decline of the popularity of the theory of ground water concentration of ore, the fact of the stratigraphic restriction of the ore, confirmed by detailed stratigraphic work of Oder and Miller (8), became relegated to a minor position. The hydrothermal theory was applied to these deposits and structural features were stressed as the important geologic factors. Currier (6, p. 272) stated that "structural control of the mineralization is clear." The breccias were believed related to bedding plane thrusts, and the coincidence of the main stope directions (at Mascot) with a system of minor faults (6, p. 274) implies that the deformation of the country has controlled the ore deposition. Brokaw and Jones (2, p. 160) stated, "Structural and stratigraphic features are recognized as important parts of the geologic control, but fracturing is the only one of these that has more than secondary importance in determining trends of mineralized zones." Crawford (5, p. 411) wrote that "tear faults or fissures at an acute angle to the bedding are vital structural features controlling the ore."

Ohle (11, p. 877) stated that although the main ore trends are invariably lines of structural deformation, there are certain limestone beds into which the ore solution has spread laterally, in adjacent unbroken ground. He calls attention to the nature of the country rock with his studies of rock permeability, and thus refocusses attention on the stratigraphic restriction of the ore deposits.

The increased exploration and development of the Mascot-Jefferson City district in the past ten years have resulted in the accumulation of many new facts on the geology and ore occurrence of the district. Notable in this respect is the increased awareness by district geologists of the sedimentary features of the host rocks. Early in the exploration program of The New Jersey Zinc Company, W. H. Callahan, Manager of Exploration, pointed out the significant influence on ore deposition exerted by certain sedimentary characteristics of the Kingsport. The present paper describes some of these features and presents some interpretations which, with their implications, are regarded as working hypotheses.

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The writer is grateful to the management of The New Jersey Zinc Company for permission to publish this paper. The views expressed,

however, are his own and do not necessarily reflect a consensus of the Zinc Company geological staff.

## GEOLOGIC SETTING

The Jefferson City-Mascot district is in the central part of the Valley of East Tennessee, part of the Appalachian Valley and Ridge province. The dominant structure of the Valley is a series of sub-parallel sheets or belts of rock, thrust up on southeast dipping faults which may be traced on strike for many miles. The structure of the belts is homoclinal, though in some places anticlines and synclines are formed. Approximately the same beds are exposed in adjacent belts.

Within the district there is folding and doming which is rare in East Tennessee. Two anticlines are revealed on the geologic map, (1) the Cherokee anticline, trending N 35° E and the Rocky Valley anticline, trending about N 65° E. There is also an apparent alignment of doming bearing about N 85° E marked by a doubly plunging anticline or elongated dome

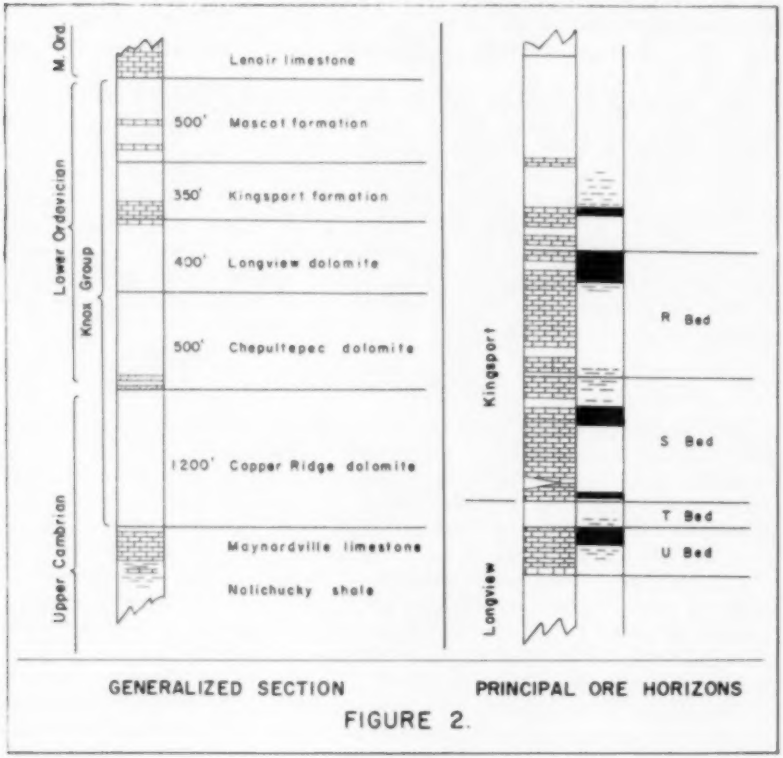


FIGURE 2.

east of Mascot and gentle doming in the vicinity of South Friends Station, about midway between Mascot and New Market. Bedding throughout most of the district ranges from nearly flat to 15 degrees southeast.

The Rocky Valley (Koppick Knob) thrust fault is a conspicuous feature of the district (Fig. 1). The fault plane dips gently to the southeast nearly parallel to bedding but the strike of the fault plane makes a low angle with the strike of the beds. The fault appears to die out in an anticline to the northeast and in several strike faults to the southwest. Dip-slip displacement along the fault thus ranges from a few feet to more than twenty thousand feet. Both shafts of the Jefferson City mine of The New Jersey Zinc Company collared in the hanging wall of the Rock Valley fault. Both reveal Upper Cambrian Maynardville limestone thrust over Lower Ordovician Mascot dolomite, a stratigraphic displacement of about 3,000 feet.

The ore deposits of the Jefferson City area are confined to the upper Longview and the lower Kingsport formations of the Upper Cambrian-Lower Ordovician Knox group (Fig. 2). The stratigraphy of these beds as well as formations above and below has been described by Bridge (1). Oder and Miller (8) have described in detail the portion of the section encountered in mining. The locations of the principal horizons within the ore-bearing section at Jefferson City have been described by Crawford (5).

The Kingsport consists of an upper 200 feet of fine-grained dolomite and a lower 100 feet of limestone with minor interbedded dolomite (R and S beds of Crawford). The uppermost part of the Longview formation consists of a fine-grained dolomite bed (T bed) about 11 feet thick, underlain by a 20 foot limestone bed (U bed), which is in turn underlain by cherty dolomite of the V Bed.

The Jefferson City mine of The New Jersey Zinc Company is located about 1½ miles downdip from the outcrop of the Kingsport formation. Bedding strikes about N 25° E and dips 5° to 10° southeast. Only a few faults have been encountered in mining to date, all of them steeply dipping normal faults, the largest of which has a displacement of about 8 feet. Local gentle warps are superimposed on the regional dip.

## ORE DEPOSITS

The mineralogy of the Jefferson City mine is simple. The ore consists of a very low-iron sphalerite in a dolomite gangue. The sphalerite averages about 0.30% Fe but a few pods of darker sphalerite containing up to 1.25% Fe have been found. There is a recoverable amount of cadmium in solid solution with the zinc, but this is visible as greenockite only rarely, as oxidation of the ore at present mine depths is uncommon. No galena has been found in the mine and it is encountered only rarely in the district. Fluorite crystals are sometimes found in vugs. One occurrence of barite in a vug has been observed.

The ore is of two types: replacement and open space filling in coarse crystalline dolomitized limestone; and, fracture-filling in brecciated fine-grained dolomite. Replacement-type ore is generally of higher grade and of greater continuity.

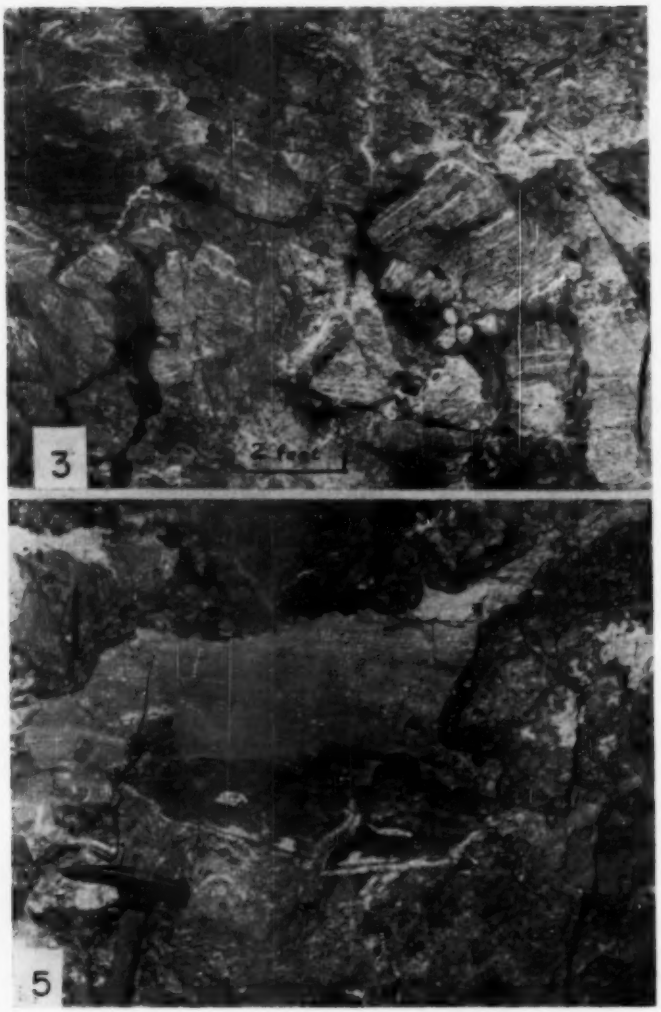


FIG. 3. Coarse dolomitized limestone breccia. Beds above and below are undisturbed. Well-mineralized, though light yellow sphalerite is hardly discernible in photograph. Area of face about 12 feet wide by 10 feet high.

FIG. 5. Vug-filling sand. Colloform sphalerite lining former void. Note grains and fragments of sphalerite and dolomite incorporated in sand. Attitude of laminations parallels country rock bedding.

Typical ore bodies of the replacement type consist of masses of completely dolomitized limestone with abundant sphalerite and white coarse-grained gangue dolomite permeating the mass. Replacement textures of sphalerite in coarse crystalline dolomite rock are common. In addition, bands and layers

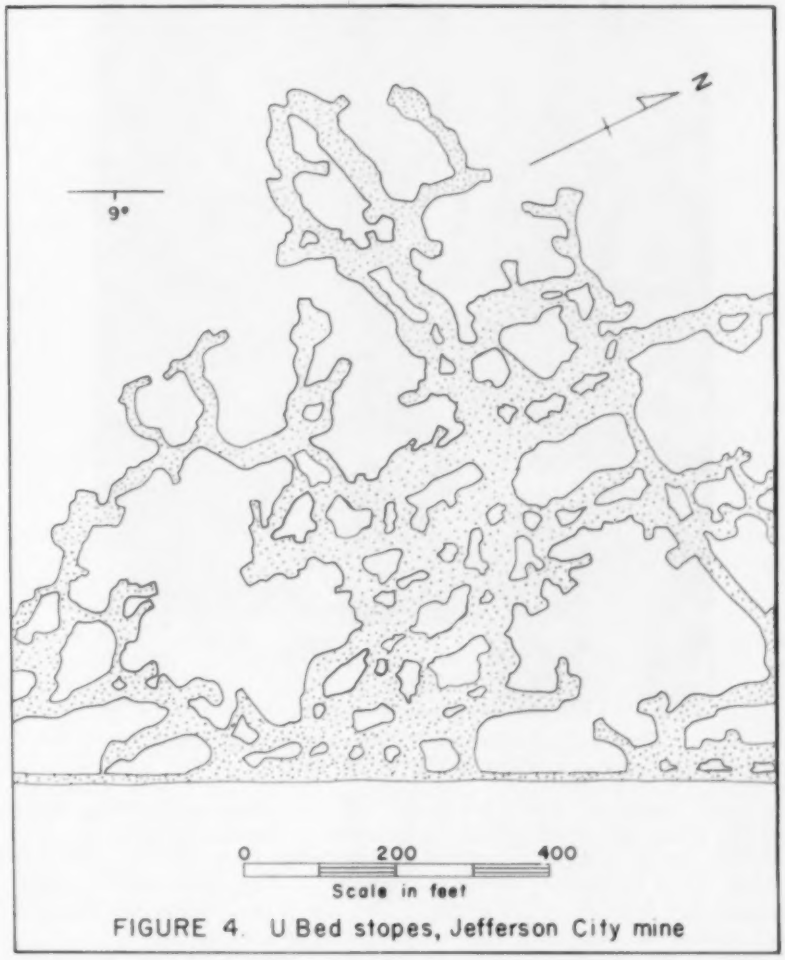


FIGURE 4. U Bed stopes, Jefferson City mine

of sphalerite up to several inches thick are common suggesting deposition in open ground.

The margins of the replacement bodies are marked by an abrupt change from dolomitized limestone to unaltered limestone. The actual contact is

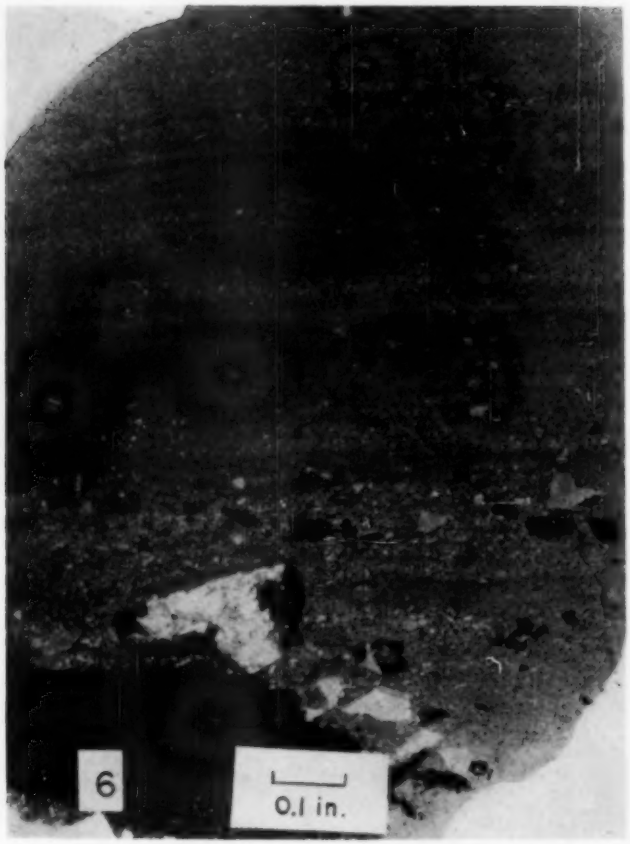


FIG. 6. Vug-filling sand. Thin section, plain light. Darker grains are sphalerite.

ordinarily gradational over a few inches with dolomitization extending along bedding planes and stylolites into the limestone. Characteristically there is a concentration of dark shaly material at the contact, apparently the insoluble residue which was ejected during dolomitization. The richest ore in a body is commonly found near the contact. For this reason mining is clean and in a worked-out stope little remains but barren limestone walls.

Within the dolomitized limestone mass the limestone has been completely altered. The rock is generally broken into a coarse breccia of lumps of coarse-grained dolomitized limestone, only slightly disoriented, suspended in a matrix of dark grey, banded dolomite. Near the base of these ore bodies the dark matrix dolomite occupies fissures cut into the lower beds, producing

a pseudoconglomerate texture with knobs of dolomitized limestone still attached to their base (Fig. 3).

The replacement-type ore shoots are from a few feet to 30 or 40 feet across and up to 15 feet high. They extend for several hundreds of feet in length and are cross-connected with parallel shoots a few tens of feet away. The mine map (Fig. 4) thus shows an elongated network of openings, the walls of which are barren limestone. Brecciation has accompanied and followed the mineral deposition for the sphalerite bands are broken and disoriented into fragments as much as several inches long. The overlying fine-grained dolomite beds have been fractured in varying degrees ranging from mosaic or "domino" breccias where the fragments are small and displacement is slight, to rubble breccias where the breaking and displacement is considerable. Replacement of the fine dolomite rock is nil and mineralization is confined to the fractured ground which ordinarily dies out within a few feet in the overlying bed. The broken fine-dolomite blocks are generally displaced downward, slumping into the ore body below. This slumping has been termed "foundering" by Odel (quoted by Oder and Hook, 9, p. 78), who attributed it to solution and removal of part of the underlying rock in the mineralizing process.

The fine dolomite beds overlying the replacement-type ore bodies, although locally brecciated immediately above the ore bodies, are in general quite undisturbed. Even where brecciated, the breaking dies out upward within a few feet, and at many localities the overlying beds are unbroken across the top of the ore bodies. Similarly, the footwall beds are not disturbed by faulting or warping. In a worked-out stope, with barren, undisturbed limestone walls, and similiarly barren and undisturbed foot- and hanging-walls, there is no evidence of fault or fracture control of the mined-out replacement-type ore body.

In two localities large volumes of fracture-filling type of ore have been discovered. In these two localities fracturing and faulting apparently localized by masses of fine-grained sedimentary breccia have cut through more than 100 feet of the S, R, and higher beds, as well as part of the sedimentary breccia body itself. These fractures are mineralized, forming ore bodies of considerable vertical dimension and as yet unknown horizontal dimensions.

*Vug-filling Sand.*—In high grade ore of the replacement type there is commonly a sand-like material filling former vugs (Fig. 5). The detrital nature of the material is obvious and the term "sand" has been applied. The sand is generally light gray to almost white and is made up of particles of dolomite and sphalerite. Locally the sphalerite content is high enough to impart a yellowish cast to the sand. The sand is deposited in alternately dark and light layers from a few hundredths to a few tenths of an inch thick. Characteristically there is graded bedding (Fig. 6).

Fragments of dolomite and sphalerite from the walls of the former opening are common and appear to have been incorporated simultaneously with the deposition of the sand. These fragments range from pieces only slightly larger than sand grains to pieces several inches long. Masses of this sand as much as four feet across have been encountered, persisting more or

less interconnected through hundreds of cubic feet of rock. Most exposures, however, are a foot or less in each dimension. Contortions and warping of the bedding are common in small exposures but in the larger exposures bedding is remarkably regular. The sand is clearly post-ore in age. The sand and included material indicate that deposition of the sphalerite in vuggy dolomitized limestone was followed by brecciation and then deposition of the sand. The sand has not been found brecciated nor cut by later fracturing.

The sand is believed to have been formed by the grain-by-grain release of particles of dolomite and sphalerite by late solutions that were capable of some intergranular solution. The material was held in suspension until deposited in the masses now visible. The source of the sand-material was nearby, for the color and composition of the sand are dictated by the surrounding rock.

The most significant observation with respect to this sand is that the laminations are parallel to the strike and dip of the country rock. It is not always possible to determine this with certainty as most exposures are too small and in these smaller masses the original bedding is commonly slumped and contorted, but in the larger exposures it has been repeatedly established.

The parallelism of the bedding of the rocks and the sand laminations indicates that the rocks were horizontal when the sand was deposited. The sand is post-ore in age, and thus it follows that the ore was deposited prior to the tilting of the rocks. The sand provides a means of dating the emplacement of the ore relative to the deformation of the country. The commonly accepted date of the mineralization is post-Appalachian orogeny, but the evidence of the sand indicates that ore deposition is much earlier.

*"Pebble"-filled Vugs.*—Mining in the replacement-type ore horizons frequently exposes vuggy ground. The vugs are normally small, on the order of a few inches in longest dimension, but the rock immediately adjacent is generally very porous with many small openings. The vugs are always in dolomitized limestone, never in limestone, and are lined with crystals of sphalerite and dolomite. Many of the larger vugs contain fragments of sphalerite or dolomite rock that are loose or only lightly cemented together. These fragments in some instances nearly fill the void. A peculiarity of the fragments is that they are generally rounded and their surfaces are highly abraded (Figs. 7, 8). The vugs and "pebbles" most nearly resemble the effects that would be produced by tumbling fragments in a small mill. The fragments are abraded, not merely corroded, and the scars on the vug walls also indicate that physical abrasion was active.

The fragments are as much as a few inches in diameter. When cracked open the sphalerite "pebbles," which are more rounded than are the dolomite fragments, exhibit radial crystalline growth, indicating that the shape of the mass was more or less round from the beginning. Possibly they originate as sub-spherical masses growing from a projection within the opening, are later loosened from their seat by solution or physical breaking, and then are free to roll around and abrade themselves and the walls of the chamber. The abrasion, however, has accentuated the rounding and has removed the protruding crystal forms and in some places has even produced a dull polish.

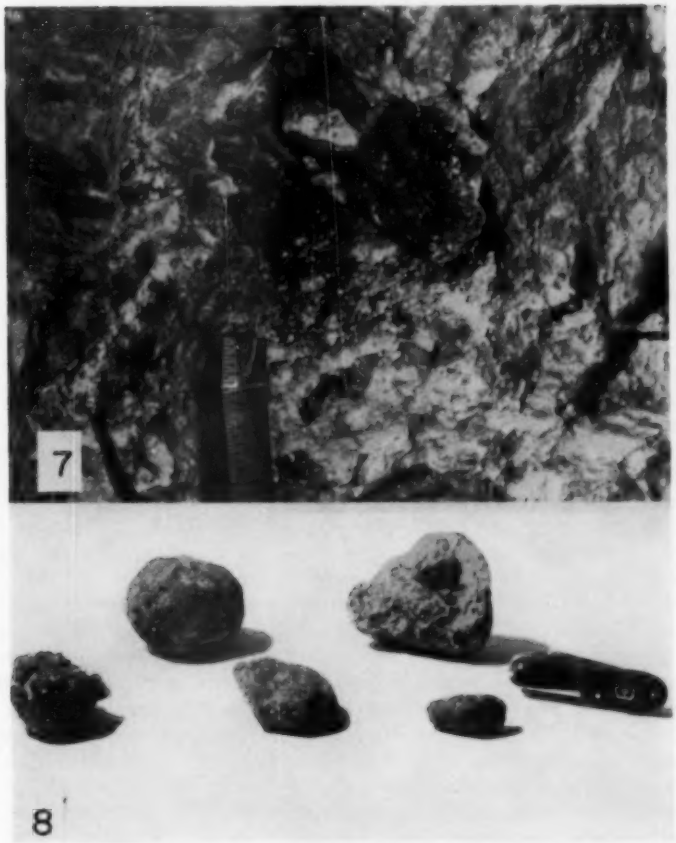


FIG. 7. "Pebbles" of sphalerite and dolomite in vug in coarse crystalline dolomite.
FIG. 8. Large "pebbles" of sphalerite from vugs in coarse crystalline dolomite.

The vug walls are likewise abraded in places. It is apparent that the abrasion of these fragments has taken place later than the emplacement of the sphalerite and dolomite crystals. Coarse dolomite crystals have been deposited on the sphalerite crystals and both have been abraded.

## SEDIMENTARY FEATURES

*Reefs.*—In the limestone horizons, particularly in the U bed, occur masses of banded dark and light gray coarse dolomite, surrounded on top and sides by limestone (Fig. 9). The alternating dark and light bands within the body,

mostly less than an inch in thickness, are flat or convex upward. The sides of the bodies are steep to vertical and in a few instances the upper portions of the sides are overhanging. The bodies terminate downward on fine-grained dolomite beds. The limestone generally has a steeper dip in the few inches immediately adjacent to the contact, suggesting slumping or compaction of the limestone against the more competent dolomite body. A foot or so away the limestone bedding is not disturbed, indicating that the slump structures are formed prior to lithification.

These bodies are from a few feet to 10 or 15 feet across and range up to a height of 6 feet. In plan they have considerable length, and form interconnected networks that enclose limestone pillars or islands from a few feet to several tens of feet across. Although no fossil forms are detectible, the general shape and appearance suggest an organic origin. They are tentatively termed "stromatolite reefs" and are ascribed to algal activity.

Characteristically the reefs possess a cap of sphalerite in a solid layer from an inch to a foot or more thick. In many places sphalerite extends into fractures and joints in the overlying limestone for a few inches. The dolomite of the reef is unmineralized, and the limestone contacts on the sides of the reefs are barren. In many places solid bands of sphalerite at the top of the reef have been brecciated into rectangular or tabular fragments up to several inches long.

Mining experience has shown that these reefs are excellent ore guides. Although locally an individual reef may be narrow and the sphalerite cap only thick enough to make mining marginal economically, these conditions generally change quickly as the headings are advanced. Branching of the reefs is common and frequently the mining operation is led into large ore bodies of good grade. On the flanks of the areas of strongest mineralization in the mine the reefs are simple and discrete in structure. Near the best ore bodies the reefs are more complex structurally and lose their simple outlines. Dolomitization of the surrounding limestone is complete and blocks of this rock are incorporated in the mass. Within the ore bodies the reef structure is generally obliterated by the mineralization but masses of dark banded dolomite, similar in appearance to the core rock of the simple reef are common (Fig. 3).

*Coarse-Matrix Breccia.*—Practically all of the ore in the coarsely dolomitized parts of the U, S, and R beds occurs in a breccia composed of blocks of coarse dolomite suspended in a matrix of coarse-grained dark gray dolomite. The general appearance of these ore shoots has already been described (Figs. 3, 4).

In the past these ore-bearing breccias have been interpreted as fault-controlled ore shoots, with accompanying wall-rock alteration. The blank walls of worked-out stopes, together with the undisturbed hanging-and foot-walls fail to reveal any through-going tectonic features that have localized ore. Further, the network pattern of reefs and coarse-matrix breccia is not easily explained as tectonically controlled.

The detached blocks of coarse dolomite are not far out of place and are

seldom more than slightly rotated. Chert beds though disturbed, can usually be traced across the breccia mass into undisturbed rock in the stope walls. These facts argue against a cut-and-fill structure such as stream channel or cave.

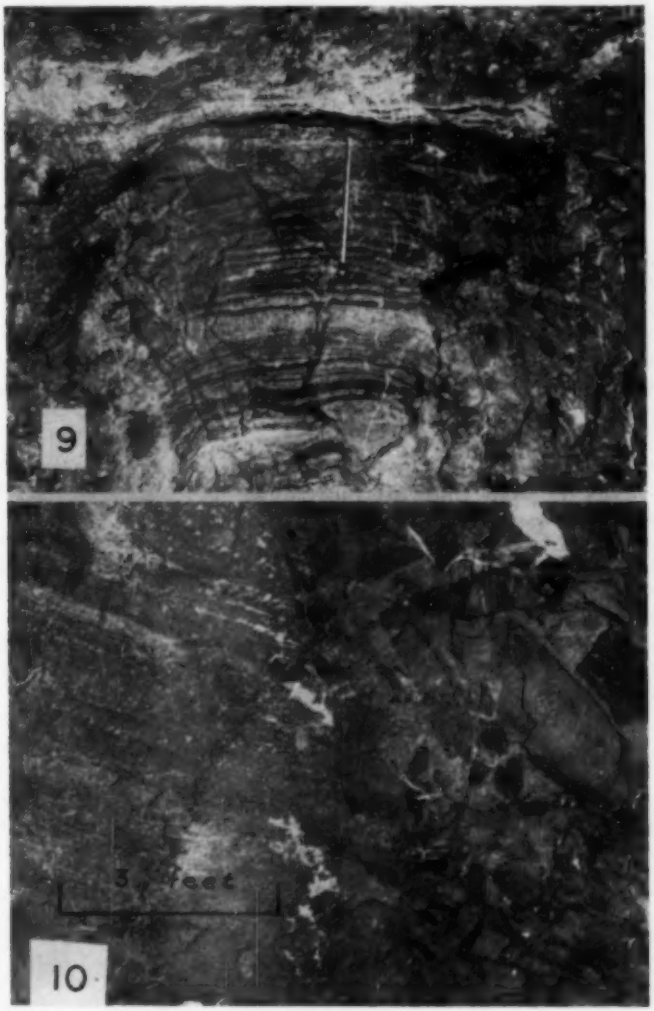


FIG. 9. Reef in U bed. The coarse dark dolomite of the reef mass is surrounded by limestone. Note thin sphalerite cap. Tape is extended about 1 foot.
FIG. 10. Fine-matrix sedimentary breccia on right, cross-cutting partially dolomitized limestone.

The breccias are believed to be sedimentary structures related to the deposition and diagenesis of the limestone. The matrix material draped around blocks and fragments of rock, and filling fissures in the underlying bedrock is identical to the "core" rock of the reefs. In fact, the coarse-matrix breccia mass seems to be the fullest development of the reef structure.

*Fine-Matrix Breccia.*—Two large bodies of sedimentary breccia have been encountered in the mine, and similar bodies are known in other mines of the District. The breccia consists of fragments of fine dolomite ranging in size from an inch or so to several feet in diameter, held in a matrix of fine dolomite (Fig. 10). There is crude stratification in the matrix material but bedding is generally strongly warped and locally draped around fragments. Sand grains and chert fragments are common locally in the matrix. Shaly material is present locally. The matrix ranges from gray, through shades of green, and locally red. Coarse crystalline dolomite fragments have been found only rarely. Where they have been seen they have apparently moved only a very short distance. Limestone fragments have been found only near the base of the breccia bodies.

In many exposures the dolomite fragments, owing to characteristic colors and textures, can be positively identified as to bed of origin. In every instance the fragment has originated from a bed above the point of observation, in some cases more than 50 feet higher.

The breccia bodies appear to be long (hundreds of feet) relative to their cross-section dimensions (tens of feet). The walls of the bodies are irregular but steep in cross section and generally straight in plan. Where the bodies crosscut limestone the contact is marked by shaly material derived from the shale partings of the limestone. The shale is strongly contorted, and the adjacent limestone shows evidence of flow. At a few localities the limestone has been dolomitized at the contact zone, but generally the limestone is unaltered chemically.

The breccia bodies encountered in the Jefferson City mine terminate downward in the U bed, though in other localities they apparently extend to a lower horizon (G. C. Ruskell, personal communication). The base of the bodies is marked by irregular dike-like masses of breccia from an inch to several feet in width filling fissures in the limestone. At and near the base, there is generally considerable limestone in the breccias, consisting of sub-angular fragments that are obviously not far from their original position.

These breccia bodies are believed to be of sedimentary origin. The shape of the bodies suggests steep-walled channels filled with rubble from the walls, cemented in a shaly and sandy dolomite sediment. The virtual absence of limestone and of coarse-crystalline dolomite in the bulk of the breccia mass suggests gradual solution and erosion that dissolved these materials. Undercutting of beds of less-soluble fine dolomite may have caused them to break and fall into a developing channel.

Other interpretations of these breccia masses have been made. They are probably similar to those interpreted by Ulrich (15) as cave or sink-hole breccias. One theory (A. D. Hoagland and Johnson Crawford, personal

communications) would relate the caves to an ancient land surface corresponding to the unconformity between the Lower and Middle Ordovician.

Some features of the matrix material suggest flowstone but one difficulty is that the matrix material is dolomite, not calcite. It would seem difficult to convert the "flowstone" to dolomite without also dolomitizing the enclosing limestone. No stalactities, stalagmites or other "cave formations" have been found. If these breccias are assumed to occupy ancient caves, a more acceptable explanation of the fine-grained matrix, with irregular sandy beds, local shaly layers and crude stratification is that this material represents an original muddy deposit washed into the developing cave.

This type of breccia is known as "dry breccia" in the district because it is ordinarily barren. The only places where it is ore-bearing are where the breccia mass is cut by later fractures that are filled with sphalerite and gangue dolomite.

As an indirect ore control, however, the breccia appears to be of considerable importance in two locations discovered to date. Immediately adjacent to the breccia masses, but not co-extensive with them, there is a zone of strong fracturing and some faulting of small displacement. This fracture zone extends through the stratigraphic section for as much as 100 feet and in some places is mineralized through its extent, forming ore bodies of considerable vertical dimension but lesser horizontal extent. Owing to the limited mining of these ore bodies to date, structural relations are not clear, but it appears that the sedimentary breccia mass, forming a discontinuity in the section has localized fracturing and faulting and indirectly provided a locus for ore deposition.

*Dolomite.*—Dolomite of many types of origin is found in the environment of the orebodies. Several of the beds in that part of the stratigraphic section normally involved in mining are fine-grained, light gray dolomite, which is locally termed "primary" or "syngenetic" dolomite. Conspicuous in the vicinity of ore is the coarse-grained dolomitized limestone known in the district as "recrystalline." Intermediate in grain size between these two are beds of medium crystalline dolomite. Gangue dolomite accompanying and following the sphalerite mineralization is common, and late tension cracks cutting mineralization and country rock alike are filled with dolomite. Dolomite is ubiquitous and it is difficult to decipher the relations and the significance of the various types and ages of dolomite.

The fine-grained dolomite beds of the Kingsport are found principally in the upper half, but a few three to five foot beds are encountered in the lower half. They are noteworthy for their great lateral extent in comparison with their thickness. Generally the beds are medium to light-gray, although a few are conspicuous by their dark color. The colors and textures of these beds are remarkably consistent through their occurrence. They make excellent key beds. Many of the beds contain faint wavy lines that seem to represent former shale partings, all but obliterated. Mottling is common and is generally distinctive of individual beds. Some beds are characterized by augen or patches of white dolomite several inches apart and up to an inch in diameter. Sand grain beds are common, especially at or near the base of

the beds. Certain of these fine-grained dolomite beds are characterized by distinctive chert. The chert occurs as discrete nodules arranged parallel to bedding or as continuous beds, up to a few inches in thickness and with smooth or irregular contact surfaces.

These fine-grained dolomite beds are considered primary or penecontemporaneous dolomite, although the recognition of strictly primary dolomite, precipitated as such from the sea water, may not be possible. Beds of fine-grained dolomite containing mottlings and faint banding suggestive of former shale partings and sedimentary structures are more clearly altered limestone beds, but the alteration seems to have been very early and probably penecontemporaneous with deposition (cf. Cloud and Barnes, 4, p. 91–94). Their great lateral extent and their occurrence interbedded with large thicknesses of limestone is suggestive of slight but widespread changes in depositional conditions that produced fundamental differences in the sediments. The common occurrence of sand grains at the base of the fine-grained dolomite beds may be indicative of a changed environment of deposition.

The coarse dolomite is clearly a replacement of limestone. Bedding, shale partings, and chert horizons can be traced from unaltered limestone across masses of coarse dolomite and into unaltered limestone. The contact zone between the coarse dolomite and limestone is ordinarily marked by stringers and veinlets of dolomite extending into the limestone, utilizing stylolites, tiny cracks, and other minute openings in the limestone for access. The network of dolomitization becomes less distinct until within a foot or two from the main body of dolomite, the limestone is unaltered. In some places at the contact of limestone and dolomite a concentration of dark shaly material up to an inch across is found. This apparently is the residue from the stylolites and shale partings, moved ahead of the advancing dolomitization.

The coarse dolomite is generally mottled or speckled in appearance, the larger grain size and colors of different particles combining to give a distinctive texture. Spots or augen of white dolomite up to 1 inch across with a dark line at the base are common and where found generally formed parallel to bedding. This dark line may represent impurities of the original limestone which were ejected from the crystallizing dolomite.

The coarse dolomite is believed to be of late-diagenetic origin, the coarse grain size suggesting that dolomitization proceeded slowly. In comparison with the uniform widespread fine-grained dolomite, the coarse dolomite occurs as patches and networks within the limestone beds. The extensive study and drilling of the Kingsport in recent years has shown that coarse dolomitization is a sedimentary feature much wider in extent than ore deposition or tectonic disturbance. Ore-related dolomitization of the limestone, is believed to be relatively minor.

*Hypotheses of Origin of the Ore Deposits.*—As already mentioned, theories of origin have ranged from sedimentary to hydrothermal over the years, changing with the accumulation of data and with the changing ideas in geological science. Mississippi Valley-type deposits, to which type the Mascot-Jefferson City district belongs, present unusual difficulties in interpretation and understanding. In an important paper Ohle (12) has summarized the

prevailing ideas and pertinent facts, emphasizing the characteristics common to Mississippi Valley-type deposits in order to arrive at a unified theory of origin. It is evident from his study that the evolution of ideas seen here has taken place in nearly all of the districts of similar ore deposits. No theory has yet been advanced that accounts for these deposits satisfactorily.

The hydrothermal theory, postulating mineralizing solutions arising from a localized source and depositing metals in favorable loci within the host rocks has considerable appeal. Such an origin is demonstrated in many districts of the world, and several of the features of the ore deposits at Jefferson City fit neatly into such a theory. The migration of sphalerite into fractured fine-grained dolomite beds; the sand-filled vugs and "pebbles" of sphalerite; the "founder" breccias, all are easily explained as the product of invading hydrothermal solutions.

Some facts that seem difficult to explain by the hydrothermal theory, however, are the remarkable stratigraphic restriction of the ore, the simple mineralogy, the low temperature of deposition, and the lack of apparent inlets. In spite of the occurrence of several horizons of identical lithologic types in the Knox dolomite, virtually all of the commercial production has come from about 150 feet of the Kingsport-Longview section. Extensive geochemical prospecting has also brought out this restriction. Permeability and porosity studies by Ohle (11) have shown that coarse crystalline dolomite, with relatively great porosity, would be the expected host rock. Yet below the favorable horizon there are many occurrences of identical beds in the Copper Ridge, Chepultepec, and Longview formations that are not mineralized. If it is true that dolomitization of the limestone was produced by a phase of the ore solutions (11 p. 888), it is difficult to understand why limestone with the lowest permeability was selected for alteration and mineralization. Hypothetical properties such as "an inherent ability to change to recrystalline" (11, p. 892) must be called upon to explain the stratigraphic restriction.

The lack of visible inlets for the migration of hydrothermal solutions from depth is cause for some embarrassment to the hydrothermal theory. The prominent Rocky Valley thrust fault would seem to be an obvious access, yet recent drilling totalling several hundred penetrations of this fault plane and associated fractured and disturbed ground beneath the fault has failed to reveal evidence that the fault is mineralized or is a likely access for migrating solutions. Oder (10, p. 53) believes that the Rocky Valley fault may be younger than the zinc mineralization.

The simple mineralogy, the low temperature of deposition and the complete absence of any evidence of igneous activity are "strains on the normal hydrothermal picture" (12, p. 786) and compel the postulation for ore deposits of this type of an igneous source "at great depth (with) no especial tendency to move upward" and "emitting over its entire area mineralization of amazing uniformity" (12, p. 786).

In some respects it seems more satisfactory to acknowledge the prominent sedimentary features in the ore horizons such as the reef structures, the sedimentary breccias, and the cyclical or rhythmic repetition of the ore horizons and intervening barren beds. These features and the evidence indicating a

very early age of the mineralization, permit a theory of origin related to the sedimentation. An obvious source of the zinc is the sea.

Work recently published by Krauskopf (7) suggests that zinc is easily removed from sea water by absorption, especially by organisms. The enrichment factor for brown algae is 400-1400 times, and the average enrichment factor for 9 marine animals is 32,500 (7, Table 9). Other workers, notably Cannon (3, p. 161) have reported that algae have the capacity to absorb zinc, concentrating it by a factor of several hundred times. She believes that the widespread zinc in the Lockport dolomite was precipitated from sea water containing uncommon amounts of metal. "An unusual source of these elements, perhaps of volcanic origin, is implied" (3, p. 162).

Extraction of zinc from the sea by marine organisms suggests the reason for the purity of the mineralogy of these deposits: preferential absorption could be highly selective. Subsequent conversion of the zinc from ion or organo-metal complex to zinc sulfide could be accomplished during burial. The temperature required is probably easily produced by compaction and burial.

A simple syngenetic origin of these deposits explains the cyclical repetition of ore horizons with repeated lithologic types within the ore-bearing formation more satisfactorily than the replacement of "favorable beds" by hydrothermal solutions. It would also account for the absence of "inlets" and it might explain the sphalerite cap over the reefs. Several difficulties must be acknowledged. It cannot account for the migration of ore into fractured fine dolomite beds above the ore shoots in the limestone beds. It is also difficult to understand the restriction of the mineralization to the district while the Kingsport sea, depositing sediments identical to those found within the district was spread over hundreds of square miles. In any case, deposition of the ore was apparently early, for the evidence of the vug-filling sand points to deposition prior to the tilting of the country rocks. Indeed, some geologists (Oder, 10, p. 53; Stuart Maher, personal communication) reasoning from field evidence in East Tennessee mining districts, believe ore deposition was completed prior to Middle Ordovician time.

There is little doubt that the sedimentary characteristics of the Kingsport-Longview beds have exerted a strong influence on the deposition of the ore. There is some suggestion that the ore is of sedimentary origin, but the presence of fracture-filling ore in overlying beds requires modification of a sedimentary ore bed by later hydrothermal (though not necessarily hypogene-derived) activity.

NEW JERSEY ZINC CO.,
JEFFERSON CITY, TENN.,
*September 1, 1959*

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# STRATIGRAPHY OF THE EASTERN MESABI DISTRICT, MINNESOTA[1]

JAMES NOVOTNY GUNDERSEN

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ABSTRACT

The Eastern Mesabi district of Minnesota is economically important because of the current large scale utilization of the magnetite-bearing Biwabik iron-formation as a source of iron ore.

The Animikie group of sediments, consisting of the Pokegama, Biwabik and Virginia formations, were deposited successively over the Giants Range granite. These sediments were subsequently intruded by small diabase bodies and the Duluth gabbro. The four well-established members of the Biwabik iron-formation have been further subdivided into 22 submembers, which are briefly described.

This paper establishes the stratigraphic framework upon which the generalized distribution of minerals of the metamorphosed Biwabik iron-formation can be presented. The discussion of the metamorphic mineral paragenesis, extensive metasomatic activity and related subjects will be presented in later papers.

## INTRODUCTION

*Purpose.*—Current large-scale mining and beneficiation of the magnetic taconites from the Eastern Mesabi range has warranted a detailed stratigraphic and mineralogical examination of the district.

[1] Second of a series of five papers on the Eastern Mesabi District. Publication authorized by the Director, Minnesota Geological Survey.

According to local terminology, as well as previous publications (1, p. 442; 3, p. 1; 8, p. 1), the Eastern Mesabi range commonly implies that portion of the Biwabik iron-formation lying east of the town of Mesaba (Fig. 1). On the basis of distinctly different mineralogical assemblages occurring in the iron formation on the Main and Eastern Mesabi ranges, however, it is proposed that the arbitrary boundary between these districts should be placed about one mile east of the abandoned town of Mesaba. This paper is concerned primarily with that part of the Eastern Mesabi district extending from R 14 W to near the former townsite of old Babbitt which is the region currently under development by the Reserve Mining Company. Because the stratigraphy and mineralogy of the Mesabi range west of R 14 W is not one of the purposes of this paper, only brief comparison of the thicknesses and tentative correlation of the various stratigraphic units of the Main Mesabi district is made with those proposed for the Eastern Mesabi district. This paper represents a condensation of the chapter on stratigraphy in the writer's

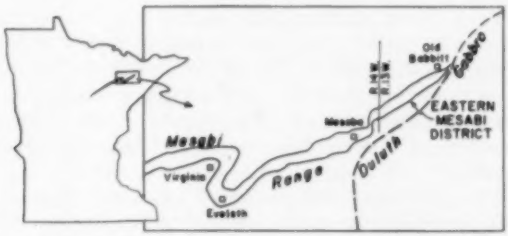


FIG. 1. Index map for the Eastern Mesabi district, Minnesota.

(6) doctorate thesis. The detailed stratigraphy of the Biwabik iron-formation and a less generalized discussion of the distribution of minerals within the formation submembers will be presented in a forthcoming Bulletin of the Minnesota Geological Survey.

The reason for delineating such a detailed stratigraphic column of the Biwabik iron-formation on the Eastern Mesabi range was to provide the necessary stratigraphic framework upon which the lateral variation of relic and metamorphic minerals within each submember could be thoroughly investigated. Although it was specifically sought, there is no field evidence to indicate that the observed metamorphic mineral assemblages are the result of variations in the initial composition of any submember. For this reason, no primary sedimentary facies could be proposed. The lateral variations in mineralogy and mineralogical assemblages within the submembers are interpreted to be essentially the result of metamorphism and metasomatism. The retrograde metamorphic mineral paragenesis, the presence of extensive metasomatic activity, and the interpretation of effects of various metamorphic events upon the iron formation will be the subjects of subsequent papers.

*Acknowledgments.*—At various times during the summers of 1955, 1956, and 1957, the writer examined cataloged drill core specimens from nearly 40 drill holes available at the Babbitt works of the Reserve Mining Company.

Extensive artificial exposures revealed in the Peter Mitchell open pit near old Babbitt were also available for detailed study. The writer is further indebted to the Reserve Mining Company for providing the Minnesota Geological Survey with three new deep drill hole cores, each of which yielded the complete or nearly complete stratigraphic sequence present in the Eastern Mesabi district. This study was supported, in part, by the Reserve Mining Company Research Fellowships for the years 1955 to 1957 and, in part, by the Minnesota Geological Survey, Dr. G. M. Schwartz, Director.

The Erie Mining Company, whose current taconite mining operations are west of R 14 W, also generously permitted the writer to log and sample core from an important drill hole located nearly one half mile east of the abandoned town of Mesaba.

The writer particularly wishes to thank Professors G. M. Schwartz, J. W. Gruner, and S. R. B. Cooke of the University of Minnesota for their active participation and personal encouragement throughout all stages of the study of the geology of the Eastern Mesabi district.

*Previous Work.*—The stratigraphic position and stratigraphy of the Biwabik iron-formation has been discussed in detail recently by several authors, notably Gruner (5), Grout, et al. (4) and White (8). They have reviewed and discussed the numerous earlier classical papers concerning the general geologic features of the Mesabi range. The papers of the authors listed above should be consulted for specific information and bibliography of the Mesabi range in general.

Broderick (1) and Grout and Broderick (4) have made significant contributions to the interpretation of the geology of the Eastern Mesabi district. They made a detailed surface study of the entire area in 1917 shortly after an extensive forest fire had revealed excellent exposures of outcrops in the district. Some small open development pits and core from several drill holes were also available for their inspection. The writer was extremely fortunate to have had the original field notes, sketches, samples and thin sections of these earlier workers available to him.

During the early phases of the study, reference was not made to previous stratigraphic investigations of the Biwabik iron-formation. Instead, pit exposures and the core from many drill holes were studied in an attempt to find as many recognizable stratigraphic units as possible. The resultant column presented in this paper is similar to that already proposed by Broderick (1, p. 444) and Grout and Broderick (3, p. 17), except for minor differences in the overall thicknesses of some of the stratigraphic units. Because of this close agreement and easy correlation between units, as well as the ideal conditions under which they worked, the earlier geologic map of Grout and Broderick could not be extensively improved upon and only minor changes in their map have been made.

*Present Work.*—Although many natural outcrops and some strata exposed by surface stripping of glacial drift were studied, most of the geological interpretation of this area was based upon features present in numerous drill core specimens and artificial exposures of the iron formation in the Mitchell pit.

FIG. 2. Generalized geologic map of the Eastern Mesabi district, Minnesota.

The Biwabik iron-formation on the Eastern Mesabi range is subdivided into 22 submembers, usually called units herein. It is not intended that the submembers described below should serve as a substitute for the units proposed by Grout and Broderick or the more commonly used Slaty and Cherty member terminology of Wolff (9, p. 142). The proposed column is in a sense academic in that some submembers are only subtly different from one another. The submembers are recognized primarily by the distribution of magnetite which most commonly occurs in some sort of layered arrangement of grains, especially as lamellae and thin beds. In this paper, the matrix in which the magnetite grains are distributed, as well as the interbedded nonmagnetic layers, are always understood to be quartzose. In most submembers, however, the magnetite- and quartz-bearing layers commonly contain traces to appreciable amounts of silicates whose distribution will be discussed in the descriptive text of each submember. In some places, the presence of a quartzose or silicate-rich matrix helps to distinguish between adjacent submembers. Some of the magnetite-rich layers are uniform in thickness but other layers commonly pinch and swell laterally. Some individual layers are regularly bedded and subparallel to one another and others are irregularly bedded and thus have a 'wavy' bedded aspect. Magnetite-rich pebbles of intraformational conglomeratic beds and magnetite-rich quartzose granule structures (described below) are also striking lithologic features of the quartzose layers of many submembers of the formation. Upon close inspection, nearly every type of magnetite-rich structure or layer can be found in most of the submembers. Fortunately, however, the lithology of a given submember can usually be recognized by its homogeneity or dominance of a particular distribution of magnetite and silicate layers within it. Some submembers are even recognized by their characteristic heterogeneity. Most of the contacts between

the submembers are gradational and hence have often been located subjectively.

## GEOLOGIC SETTING

The chronologic and stratigraphic sequence in northern Minnesota is best summarized in Table 1, as adapted from White (8, p. 3) after Grout, et al. (4). Of the many stratigraphic units listed in that table, only the Biwabik iron-formation of the Animikie group, as it occurs on the Eastern Mesabi range, is discussed in detail below. The distribution of the rock units occurring on the Eastern Mesabi is shown in Figure 2, modified after Grout and Broderick (3).

Although somewhat complicated by minor folds and faults, the gross structure of the Animikie group of sediments is simple. The contact between the Giants Range granite and the Animikie group of sediments appears to be a nonconformity that has been slightly modified by metamorphism. The Biwabik iron-formation is concordant with the Pokegama and Virginia formations, and from the few contacts observed, it appears that these formations are

TABLE 1

STRATIGRAPHIC SEQUENCE IN NORTHERN MINNESOTA
(after White, 1954)

CENOZOIC

Pleistocene deposits (Wisconsin glacial drift)

unconformity

MESOZOIC

Upper Cretaceous
  Colerain formation* (shale, conglomerate)

unconformity

LATE PRECAMBRIAN

Keweenawan group
  Upper
    Hinckley formation* (sandstone)
    Fond du Lac formation* (red shale, sandstone)
  Middle
    Various unnamed granites*
    Duluth gabbro
    Beaver Bay complex and Logan intrusions*
    Keweenaw Point volcanics* (flows, tuffs)
  Lower
    Puckwunge formation* (conglomerate, sandstone)

unconformity

Animikie group
  Virginia formation (argillite, locally calcareous)
  Biwabik formation (iron-formation)
  Pokegama formation (quartzite, argillite, conglomerate)

unconformity

MIDDLE PRECAMBRIAN

Algoman batholiths (Giants Range and Vermilion* granites)
Knife Lake group* (slate, graywacke, iron-bearing beds, conglomerate, with tuffs, flows, intrusions)

unconformity

EARLY PRECAMBRIAN

Batholithic intrusions* (Saganaga granite)
Keewatin group
  Soudan formation* (iron-formation)
  Ely greenstone* (flows, tuffs)

*Not locally present on the Eastern Mesabi range.

also conformable. The strike of the formations essentially follows the elongate outcrop pattern of the Biwabik formation seen in the generalized geologic map. The Pokegama formation is too thin to be clearly presented on this map but small outcrops of it occur along the northern outcrop limit of the iron formation, especially near old Babbitt. The dip of the Animikie sediments ranges from zero to about 30 degrees, mostly about 10 degrees, to the south-southeast. The gross structure of the Duluth gabbro in the region of the Eastern Mesabi district is somewhat sill-like in shape and probably dips about 30 degrees to the southeast near where it truncates the iron formation. Core from hole 1 indicates, however, that the floor of the gabbro is locally steep in at least one place.

### GIANTS RANGE GRANITE

Many outcrops of the Giants Range granite are found along the northern outcrop limit of the Biwabik iron-formation, especially near the former townsite of old Babbitt. The granite was also encountered in a few drill holes.

In hand specimen, this rock is a pink-white, porphyritic, (hornblende) biotite granite. The euhedral to subhedral phenocrysts are pink silicic feldspar (cloudy orthoclase?) that commonly exceed ½ inch in diameter. The smaller subhedral plagioclase laths are clear to milky white but are locally tinted pink due to admixtures of silicic feldspar. Neither feldspar shows sharp grain or crystal boundaries but seem to pass somewhat indistinctly into a fine-grained, biotite-rich quartzose matrix. Much of the biotite is segregated into clusters that are mainly interstitial to the feldspar grains but in many places thin streaks of biotite almost completely surround the smaller (1 to 3 mm) grains of both feldspars. In some places, the biotite is segregated into veinlet-like streaks and small biotite-rich schlieren. Some cores show pronounced gneissic foliation.

The specimens examined in thin section do not show a simple igneous texture; instead they show fabrics more closely associated with hybrid or partially metasomatized igneous rocks. The orthoclase phenocrysts are commonly clouded and subhedral in shape but their borders are irregular in detail. The plagioclase grains (about $An_{15}$) are both poikilitically enclosed within the larger orthoclase crystals or form a granoblastic-like groundmass along with quartz and orthoclase. These minerals also show irregular to nearly sutured grain boundaries. Locally the plagioclase laths have cloudy and altered cores with clear or fresh-looking rims but the grains do not show primary compositional zoning. Locally both feldspars have altered to a cloudy white material (kaolin?) and white mica (sericite?). Some plagioclase grains appear to be slightly saussuritized in some localities but in thin section these grains are seen to have been partially replaced instead by green (and some brown) biotite and secondary chlorite.

The mafic minerals of the granite are typically segregated into numerous small clusters of grains that are essentially interstitial to the feldspars and quartz. The most abundant ones are green and brown biotite both of which commonly contain many strong pleochroic haloes caused by minute, radio-

active zircon grains. In most places both biotites are partially altered to chlorite (penninite). Minor amounts of green hornblende are present and in some places this mineral exists only as remnants within locally abundant biotite. The accessory minerals zircon, apatite, sphene, magnetite and ilmenite (with some secondary leucoxene) are commonly found in the mafic mineral clusters.

A cursory examination of the granite outcrop areas seems to support the common belief that the adjacent sediments of the Animikie group were deposited nonconformably upon the slightly irregular eroded surface of a granite. Granitic pebbles and boulders within the overlying Pokegama and Biwabik formations strongly support this view, although it would be difficult to prove they did not originate in the vast granitic and metamorphic terrain a few miles to the north because of the additional presence of boulders of metamorphic rocks. On the other hand, in some outcrops the spatial relationships between the granite and the overlying sediments suggest an intrusive contact. In addition, closer inspection of the overlying formations adjacent to the granite reveals locally abundant minerals, such as andradite, plagioclase, orthoclase, hypersthene, hornblende, apatite, and biotite, that are perhaps somewhat more typical of contact-metamorphic mineral assemblages. It is probable that the Animikie sediments were deposited on an eroded granitic mass but that a subsequent metamorphic event locally affected the mineralogy and textures of the earlier granite and the immediately adjacent sediments. There is no direct evidence apparent to the writer that indicates whether this event was related or not to the igneous activity accompanying the emplacement of the Duluth gabbro.

### POKEGAMA FORMATION

There are few outcrops of the Pokegama formation on the Eastern Mesabi range and most of these suggest that the formation was deposited on an eroded granite surface. Core from the Pokegama formation was recovered in several holes, some of which extended into the underlying granite. Drill cores indicate the formation is about 30 feet thick near the western end of the area under discussion and thins to about 13 feet near the eastern end of the Mitchell pit. It is apparently missing or appreciably thinner farther east. The formation generally consists of a whitish gray quartzite but due to the local presence of fine-grained silicates some parts are distinctly greenish gray. The Pokegama formation contains locally arkosic and shaly quartzites on the Main Mesabi range. The basal beds of the Biwabik iron-formation are also quartzose but they generally have a pebbly or conglomeratic fabric and commonly contain some typical iron formation silicates and magnetite. The Pokegama formation is usually easily separated from the iron formation on the basis of its light color and lack of magnetite layers.

Many thin sections show relic 'sandy' fabrics that clearly indicate the original clastic nature of the formation. The rounded 'sand' grains are now quartz but some may have been clastic chert grains prior to recrystallization. Almost all of the grains are clear and many possess overgrowths of clear quartz. Most of the material interstitial to the clastic grains, however, is

not clear siliceous cement but normally consists of a variety of minerals. Brown and green biotite, both of which have partially altered to pale green chlorite, are the most abundant of the interstitial silicates. In some places moderate amounts of andradite, actinolite, cummingtonite and minor amounts of blue tourmaline are present. The amphiboles and the biotites locally contain many pleochroic haloes around minute enclosed zircon grains. Many pleochroic haloes are still apparent in the chlorite, secondary after biotite. Although most of these silicates are essentially interstitial, numerous clastic quartz grains have been partially to almost completely replaced by the silicates. Apatite is also locally abundant with the above mentioned silicates.

Several thin sections of the formation show few relic sedimentary fabrics because of rather complete recrystallization. Most of these specimens consist of a granoblastic mosaic of mineral grains. Xenoblastic quartz is generally the most abundant mineral present and is commonly associated with differing amounts of interstitial brown and green biotite and secondary chlorite after biotite. Many of the specimens, however, contain silicic feldspar (orthoclase?) in amounts up to 40 percent. Some of the biotites are locally concentrated in lamellae that probably reflect relic layering. In these rocks, however, the biotite fabric is distinctly decussate, rather than lepidoblastic. A few specimens contain abundant amounts of andradite, hypersthene, cummingtonite and plagioclase (oligoclase?) and traces of pyrrhotite. The amphibole, chlorite and biotite commonly contain small pleochroic haloes around minute zircon grains, as noted in specimens described above.

### BIWABIK IRON-FORMATION

The division of the Biwabik iron-formation into the classical Upper Slaty, Upper Cherty, Lower Slaty (including the Intermediate Slate) and Lower Cherty members (Wolff, 9, p. 142) has been maintained although it must be emphasized that the iron formation in the Eastern Mesabi district is rarely, if ever, slaty or cherty. In the following discussion, these names allude only to stratigraphic members and not to descriptions of rock types. Broderick (1, p. 444) and Grout and Broderick (3, p. 17) maintained the classical division of the formation but also recognized additional distinctive strata within these members. Their columnar section is presented in Table 2. The writer, however, has subdivided the formation members into many (22) submembers, commonly referred to as 'units' in the following text. The equivalence of the stratigraphic rock units proposed by Wolff and by Grout and Broderick to the submembers proposed by the writer is indicated in Table 3. The classification of the taconite rock-types included in this column has been discussed in an earlier paper (7).

On the Eastern Mesabi range, the texture of most of the rock types of the iron formation is finely granular (less than .25 mm diameter) or simply hornfelsic. Some of the taconites, however, are locally medium granular (.25 to 1 mm diameter) to coarse granular (1 to 10 mm diameter) and very coarse granular (greater than 1 cm diameter; rarely to 15 cm). These coarser fabric rocks are not foliated nor lineated and may be described as

TABLE 2

TABULAR SECTION OF THE BIWABIK IRON-FORMATION ON THE EASTERN MESABI
(after Grout and Broderick, 1919)

VIRGINIA FORMATION

| | BIWABIK IRON-FORMATION | Thickness (feet) |
|---|---|---|
| Upper Slaty | | |
| $Aub_6$ | Limy carbonate layers (less than 5% mt) | 5 to 10 |
| | Banded amphibole and white quartz in thin layers up to 6 inches thick (less than 5% mt) | 40 to 50 |
| $Aub_5$ | Taconite in thin beds mostly less than 1/8 inch thick (about 20% Fe as mt, decreasing at top) | 25 to 35 |
| | Taconite in thin beds and concretions with a granule texture, and white quartz septaria. The thin beds are drag folded and even brecciated. A zone of garnets occurs near the bottom (about 20% Fe as mt) | 40 to 45 |
| Upper Cherty | | |
| $Aub_4$ | Dark heavy taconite, with some conglomerate texture, and granules, alternating in thick beds with thick layers of magnetite (about 30% Fe as mt) | 10 |
| | Jasper and chert with algal structure and conglomerate (about 30% Fe as mt) | 1 to 10 |
| | Dark heavy taconite like the bed above the jasper (about 30% Fe as mt) | 20 to 30 |
| | Gray taconite with conglomerate and granule texture and many thinner lenticular beds of magnetite (about 20% Fe as mt) | 80 to 100 |
| Lower Slaty | | |
| $Aub_3$ | Fine massive to slaty quartz amphibolite with only obscure granule structure, and a few magnetite beds. Fayalite crystals in places (about 10% Fe as mt) | 65 |
| $Aub_2$ | Black thin bedded slate, more or less recrystallized (about 5% Fe as mt) | 25 |
| Lower Cherty | | |
| $Aub_1$ | White to gray chert with coarse algal structures (less than 5% Fe as mt) | 10 to 15 |
| | Variable taconite with some cherts, breccias, fragmental sands, garnets, etc. (from 25 to 35% Fe as mt) | 2 to 52 |
| | Basal beds; conglomerates in many places, and (in absence of Pokegama quartzite) some green shales (less than 5% Fe as mt) | 0 to 15 |
| | | 350 to 470 |

POKEGAMA FORMATION OR GIANTS RANGE GRANITE

granoblastic hornfelses, or even better as granofelses, as defined by Goldsmith (2, p. 109).

The rocks have, in general, a 'granular texture' because of the coarsened fabric produced by recrystallization. Due to the presence of small 'granule structures,' many of the quartzose layers throughout the formation may have in addition a 'granule texture.' These granule structures are generally well-rounded, sub-spheroidal quartzose masses that range from the size of coarse-grained sand to very small pebbles. They are typically oval shaped when viewed in sections cut perpendicular to the bedding planes of the rock. Most range from 0.5 to 2 mm in diameter but some small pebbles may be of identical origin. On the Eastern Mesabi, most of the granules are chert-like quartzose masses that contain differing amounts, from zero to near 100 percent, of micron-sized magnetite dust. Many relic granule structures are also preserved in places where the quartz and magnetite have been slightly coarsened by recrystallization. In a few instances, hematite (martite?) is similarly distributed within granules. Minute amounts of extremely finely divided clay-like material, resembling allophane, are apparent in many of the highly quartzose granules. Many relic granule structures are still evident in outline even where clusters of metamorphic silicates have extensively replaced these structures. Granule-shaped clusters of minute inclusions within some silicates have also been interpreted to be relic of these structures. On the Main Mesabi range, these relic granule structures are best described as masses of fine-grained silicates, especially greenalite, minnesotaite and stilpnomelane

TABLE 3

GENERALIZED COLUMNAR SECTION
OF THE
BIWABIK IRON-FORMATION
IN THE
EASTERN MESABI DISTRICT, MINNESOTA

| Members (Main Mesabi) (Wolff, 1917) | Members (Eastern Mesabi) (Grout and Broderick, 1919) | Submembers (Eastern Mesabi) (Gundersen, 1958) & (approx. thickness, feet) | Description of Submembers (Note: (east) & (west) refer to areas near the eastern & western holes) |
|---|---|---|---|
| UPPER SLATY | $Aub_6$ | A (5) | calcite marble: minor diopside, wollastonite, idocrase, andradite & quartz |
| | $Aub_5$ | B (16) | layered (diopside) chert taconite locally with ferroactinolite, hedenbergite and some cummingtonite and actinolite |
| | | C (42) | laminated (ferrohypersthene-magnetite) quartz taconite with hedenbergite & fayalite (east) & laminated (cummingtonite-magnetite) chert taconite (west) |
| | | D (7) | wavy laminated (actinolite-magnetite) chert taconite locally with cummingtonite and minor hedenbergite |
| | | E (6) | quartz taconite with abundant granule structures and locally with quartz-filled septaria structures; minor magnetite, cummingtonite and actinolite |
| | | F (20) | shaly bedded (magnetite-cummingtonite) quartz taconite with minor andradite and hedenbergite; locally abundant cummingtonite (west) |
| | | G (25) | quartz taconite (east) and mottled (andradite) quartz taconite (west) with abundant magnetite-bearing granules throughout |
| UPPER CHERTY | $Aub_4$ | H (10) | wavy layered (actinolite-magnetite) quartz taconite with minor hedenbergite; locally with fayalite (east) and cummingtonite (west) |
| | | I (5) | algal (magnetite) quartz taconite with abundant magnetite-rich granules and pebbles; conglomeratic fabric throughout; minor hematite |
| | | J (16) | granule (magnetite) quartz taconite with abundant magnetite-rich pebbles near top and thick, layered (magnetite) quartz taconite near bottom |
| | | K (35) | wavy layered (silicate-magnetite) quartz taconite with abundant magnetite-rich granules and pebbles; silicates are actinolite and ferrohypersthene (east) and cummingtonite (west) |
| | | L (30) | wavy layered (silicate-magnetite) silicate-quartz taconite with abundant magnetite-rich granules near bottom; silicates with magnetite are ferrohypersthene and ferroactinolite (east) and cummingtonite and actinolite (west); silicates with quartz are ferrohypersthene (east) and cummingtonite (west) |
| | | M (20) | layered (magnetite) fayalite-quartz taconite with ferrohypersthene (east) and layered (magnetite) cummingtonite-quartz taconite (west) |
| | | N (4) | fayalite-quartz taconite with ferrohypersthene (east) and cummingtonite-quartz taconite (west); minor magnetite |
| | | O (17) | bedded granule (magnetite) quartz-fayalite taconite with some ferrohypersthene and minor cummingtonite (east) to layered quartz-cummingtonite taconite with magnetite-bearing granules (west) |
| LOWER SLATY | $Aub_3$ | P (60) | shaly quartz-fayalite taconite to fayalite taconite (east) and shaly quartz-cummingtonite taconite to cummingtonite taconite (west); minor magnetite |
| | | | argillaceous graphite-silicate-quartz rock with abundant ferrohypersthene and minor fayalite, biotite, almandite and pyrrhotite (east) and traces of pyrite, pyrrhotite and cummingtonite (west) |
| | $Aub_2$ | Q (26) | layered (magnetite) fayalite-quartz taconite with minor cummingtonite |
| | | | layered (magnetite) quartz taconite with minor cummingtonite throughout, and hedenbergite and some fayalite (east) |
| | | | granule (magnetite) quartz taconite with minor cummingtonite throughout, and minor fayalite (east) |
| LOWER CHERTY | $Aub_1$ | R (11) | |
| | | S (8) | layered and granule (magnetite) cummingtonite-quartz taconite with hedenbergite locally, and some fayalite (east) |
| | | T (5) | |
| | | U (10) | quartz taconite with minor hedenbergite and cummingtonite; clastic quartz pebble zone locally at base |
| | | V (3) | |

[1] In units B and L the name "ferroactinolite" should read "hornblende."
[2] In unit O, "layered" should be omitted.

but granule structures composed of fine-grained chert and dusty magnetite are rare. The writer believes that the granule structures of the entire Mesabi range were probably precipitated flocs of chemical origin, somewhat resembling silica gel, that were subsequently congealed, rolled and well-sorted on the ocean floor to produce the obvious clastic fabrics that the granules and their fragments produce. A fuller treatment of the relic sedimentary structures, especially granules, of the iron formation will be given in a later paper.

For the purpose of discussion of lithologic features of the core specimens, all holes east of R 13 W including hole 21 are collectively called the eastern holes. The remaining holes are referred to as the western holes. Exceptions to this grouping will be made where appropriate. The word 'zone' implies only a 'thickness of rock,' usually displaying a particular feature. The terms 'magnetite-rich,' or 'silicate-rich,' as used in the descriptive text below are used merely as comparative terms. For example, a particular thin zone of rock containing many magnetite-bearing lamellae or magnetite-bearing pebbles may be described as a 'magnetite-rich' portion of a given specimen, which as a whole may be highly quartzose. Economically speaking, only some of the submembers, mainly from the Upper Cherty member, are actually sufficiently rich in magnetite to be amenable to beneficiation with present methods.

Most of the available drill core was obtained from the upper members of the iron formation and, in fact, during the first stages of the study cores from the entire section were not available. Consequently as a matter of convenience, the submembers are lettered in the succession that they are encountered in drilling such that the uppermost unit is submember A and the basal unit is submember V.

### *Lower Cherty Member*

On the Eastern Mesabi range, the Lower Cherty member is essentially a thin wedge of sediments that increases in thickness from east to west. Core from the member was recovered from four holes, 17, 21, 32 and 34, in which the thicknesses range from about 30 feet in the east to nearly 50 feet in the west. The member is about 136 feet thick near Mesabi but pinches out and is truncated by the Duluth gabbro to the northeast.

Because the holes are so widely separated (about two miles apart) within a formation member that varies appreciably in thickness and lithology, the proposed submembers R, S, T, U and V, are not nearly as well defined nor as well correlated as the submembers of the overlying iron formation members. There are many bedding features that occur in one or more holes and not in the others. The problem of description and correlation is made more complex by the subsequent metamorphism of the sediments. Although the other members and submembers of the iron formation are all heterogeneous in detail, they are in a sense rather uniform in their areal extent. Because of this fact, the stratigraphic units of the remaining iron formation members were relatively easily recognized and correlated from hole to hole, in spite of variations in silicate assemblages present in the core.

The Lower Cherty member appears to lie conformably upon the Pokegama

formation. The basal zone of the Biwabik formation is generally marked by a pebbly, conglomeratic zone. The member, in general, consists of poorly layered, magnetite-bearing, quartzose taconite. The upper boundary is easily identified by the normally abrupt change of rock type into the silicate-rich, magnetite-poor, dark (carbonaceous?) bottom unit of the Lower Slaty member.

*Submember V.*—This quartzose basal unit is magnetite-poor and except for the presence of granule structures and silicates that are typical of the iron formation, it locally resembles the underlying Pokegama formation. To the east, the unit is only about 3 feet thick and about 8 feet to the west but near Mesaba it reaches 30 feet.

The bottom eight inches or so of the cores of this unit are generally conglomeratic, containing many quartzose pebbles, and probably corresponds to the hematitic 'red basal taconite' of the Main Mesabi range.

The unit consists dominantly of quartz and minor amounts of magnetite. There are also minor to locally abundant amounts of hedenbergite as well as minor amounts of cummingtonite in the quartzose layers of the unit. In a few extensively recrystallized specimens, such minerals as andradite, apatite, blue tourmaline, actinolite, zircon, green and brown biotite (with secondary chlorite) are present in small amounts.

*Submember U.*—This unit contains locally appreciable amounts of magnetite, especially in granule structures and groups of lamellae. The unit increases in thickness from about 4 feet in the east to about 13 feet in the west, but is nearly 60 feet farther west near Mesaba.

The magnetite-rich granules are commonly closely packed together and somewhat segregated into layers that range up to 4 inches thick. Local concentrations of magnetite-rich lamellae also commonly form thin zones up to ¾ inch thick. The interbedded quartzose layers contain substantial amounts of silicates and range in thickness from ¼ to 12 inches but are mostly 1 to 5 inches. Hedenbergite is locally abundant along with some fayalite to the east and with increasing amounts of cummingtonite to the west. In addition to granule structures and lamellae, some clastic quartz grains also exist as primary sedimentary relics. These minor clastic zones show a fabric almost identical to that shown by parts of the Pokegama formation.

*Submember T.*—This unit averages about 5 feet to the east and 20 feet thick in the westernmost hole and is relatively rich in magnetite. It is nearly 12 feet thick near Mesaba. In a general way, the distribution of magnetite varies from abundant magnetite-rich lamellae and thin layers near the bottom to irregularly shaped zones of densely packed magnetite-rich granules near the top.

The quartzose material, in which the magnetite is distributed, contains minor amounts of fayalite in core from the eastern holes. Moderate amounts of hedenbergite and minor amounts of cummingtonite are locally present from core throughout the area. In many respects, the unit is somewhat similar to unit J of the Upper Cherty member.

*Submember S.*—This unit is similar to the overlying unit except that silicates do not dominate the non-magnetic parts of the rock. The unit is 22

feet thick near Mesaba but only averages about 8 feet thick in the Eastern Mesabi district.

The individual magnetite-rich layers commonly range from $\frac{1}{8}$ to $\frac{1}{4}$ inch thick but they are relatively few in number. The interbedded quartzose layers are mostly $\frac{1}{4}$ to 2 inches thick and commonly contain many granule structures. Algal structures, or their fragments, are present near the top of the unit in holes 21 and 32, but were not found in the other two holes.

Minor amounts of fayalite are present in core from the eastern holes. Moderate amounts of hedenbergite and minor amounts of cummingtonite are found throughout the core.

*Submember R.*—This unit contains the last magnetite-rich layers or layered zones to be deposited before the overlying magnetite-poor unit Q. The unit is rather uniform throughout and averages about 12 feet in thickness.

The magnetite-rich parts are actually few in number and generally consist of many closely spaced, lamellae that form zones $\frac{1}{4}$ to $\frac{1}{2}$ inch thick, but some range up to 4 inches.

The magnetite-rich layered zones are normally separated by 1 to 8 inches of locally silicate-rich quartzose layers. Most of this interbedded non-magnetic material consists of quartz with moderate to locally abundant amounts of fayalite, lesser amounts of hedenbergite and rarely ferrohypersthene occurring as irregularly shaped layer-like masses. Only minor amounts of cummingtonite occur regularly throughout the area. Slightly recrystallized magnetite-rich granule structures are still apparent in the quartzose layers of the unit. Traces of andradite, calcite, pyrrhotite and chalcopyrite locally associated with hedenbergite, and almandine and brown biotite associated with fayalite, are locally found in some core.

Near Mesaba, a ten foot thick transition unit, R′, lies between units Q and R. It consists of interbedded rock-types that are similar to those of units Q and R.

### *Lower Slaty Member*

The Lower Slaty member is normally uniform in thickness, ranging from 78 feet near Mesaba to about 86 feet in the Eastern Mesabi district, but is 117 feet thick in hole 17. It has been divided into two submembers, P and Q, the latter of which corresponds to the Intermediate Slate of the Main Mesabi range. Most of the exploration drill holes on the Eastern Mesabi range terminate in the upper part of submember P.

The Lower Slaty member contains less total iron and iron as magnetite than the other members of the iron formation. It is typically silicate-rich and poorly bedded throughout the area. The upper part of the Lower Slaty member, unit P, normally contains silicate assemblages similar to those near the base of the Upper Cherty member. The upper boundary is generally determined by the appearance of abundant magnetite and well defined bedding of the overlying Upper Cherty member.

*Submember Q.*—This magnetite-poor submember is much darker than the adjacent units and is easily recognized on that basis. The unit averages about 26 feet in thickness but is only 20 feet near Mesaba.

Most of the core from the western holes may be described as a massive, black, fine-grained, argillaceous, graphitic, silicate- and quartz-bearing rock, which resembles a slate except that it lacks true slaty cleavage. In many places it is indistinctly layered and the bedding surfaces of these layers have a graphitic sheen. An edgewise conglomerate is prominent near the bottom of the unit in the western holes. The pebbles consist of tabular or slab-like chert fragments. Minute amounts of cummingtonite, pyrite and pyrrhotite occur locally.

In the eastern holes, the unit is lighter in color, more distinctly layered and generally contains coarse-grained silicates. The dominant silicate is ferrohypersthene which occurs as very coarse irregular, poikiloblastic grains or clusters of grains that are normally abruptly bounded above and below by thin, dark graphite-rich layers. Minor amounts of almandite, biotite, pyrrhotite and cummingtonite occur in a few cores. The ferrohypersthene-rich layers form an irregularly alternating layered sequence with these darker, fine-grained (fayalite)-quartz-graphite-rich layers. The alternating dark and lighter layers are mostly between $\frac{1}{8}$ and $\frac{1}{4}$ inches thick and rarely reach 1 inch thick. Both layers appear to reflect primary bedding although much of the layering was modified during metamorphism.

*Submember P.*—Unit P, which is found in core from most of the drill holes, is best characterized as containing abundant ferrous silicates and minor amounts of magnetite. It is rather uniform in thickness, averaging about 58 feet near Mesaba and eastward but reaches 97 feet in hole 17.

The unit contains somewhat quartzose lamellae and thin beds in many places but is typically silicate-rich elsewhere. Fine-grained, disseminated magnetite, and possibly some graphitic material, impart a vaguely layered aspect to the silicates in many places but, as a rule, the silicate-rich parts of the core are rather massive. In several places, small zones of silicate-rich material are distinctly thin bedded.

The unit is not entirely lacking in layered magnetite because many core specimens contain a few magnetite lamellae or even laminated magnetite zones up to 2 inches thick. Some fine-grained magnetite occurs in granule structures and a few small pebbles, but most of the relic granule structures are typically quartzose. The magnetite content of the unit, however, does not exceed a few per cent.

Unit P contains an abundant variety of silicates and displays many different metamorphic fabrics among its minerals. It is the most obviously metamorphosed and recrystallized submember of the Biwabik iron-formation. Relic granule structures are still locally apparent, however, in most places. The rock in the core from this unit in hole 18 and in holes lying east of hole 17 is a medium-grained granoblastic (magnetite)-quartz-fayalite granofels, i.e., a eulysite. Minor to trace amounts of fine-grained actinolite, hornblende, cummingtonite, brown and green biotite and apatite normally occur in this eulysite rock. The fine-grained amphiboles and biotites commonly contain small pleochroic haloes around minute zircon grains. In some places, a few poikilitic porphyroblasts of cummingtonite and ferrohypersthene have developed.

Specimens of the unit from holes numbered from 19 to 26 characteristically have a mottled appearance. The mottling is produced by the presence of roundish remnants of fayalite- and ferrohypersthene-bearing mineral assemblages, similar to those noted in the eulysites to the east, within a finer grained groundmass of prismatic cummingtonite, with or without xenoblastic quartz. Minor amounts of actinolite and plagioclase accompany the fine-grained cummingtonite in some specimens.

Fine-grained prismatic to acicular cummingtonite, along with minor amounts of quartz, dominates the mineralogy of the unit in core from the remaining holes to the west. Trace amounts of fayalite remnants are found, however, in core from almost all of these holes as far west as hole 33.

### *Upper Cherty Member*

The Upper Cherty member has been divided into eight submembers; H, I, J, K, L, M, N and O. This member contains the highest percentage of total iron, as well as the largest amount of iron as magnetite and is currently being mined on the Eastern Mesabi range by the Reserve Mining Company.

The Upper Cherty member was cut by a large number of drill holes and was found to vary in thickness from about 120 to 160 feet, averaging about 140 feet, but is about 246 feet thick near Mesaba.

Most of the submembers typically contain magnetite-rich pebbles of intraformational conglomerates. In comparison to other members of the formation, the quartzose layers of the member are relatively thicker and they characteristically contain granule structures in most places. Many of the basal submembers locally contain abundant amounts of silicates.

*Submember O.*—In contrast to the adjacent units, submember O is characterized by abundant magnetite-rich granules and in some places, small pebbles. This unit is generally persistent but submembers M, N, and O could not be differentiated in core from the hole near Mesaba. Unit O ranges from 5 to 26 feet, but averages about 18 feet, in thickness.

Throughout the submember, numerous magnetite-rich granules along with some small pebbles are locally concentrated into lamellae and into closely packed, uniform to lenticular, laminated zones that range from ¼ to 12 inches in thickness. Fine-grained magnetite also occurs to a much lesser extent as lamellae and as laminated zones that reach 2 to 4 inches thick in some places. The silicate-rich quartzose matrix in which the magnetite is distributed varies greatly, mineralogically, throughout the area. Except for minor differences the distribution of fayalite, poikilitic cummingtonite and ferrohypersthene and fine-grained prismatic to acicular cummingtonite is nearly the same as just described for the underlying unit P. Minor amounts of hedenbergite, actinolite, hornblende, oligoclase and minute amounts of pyrrhotite and chalcopyrite occur locally in the unit. Core from hole 33 contains the westernmost occurrence of fayalite. Relic granule structures occurring in the eulysite portions of the unit to the east consist of nearly solid masses of fine-grained magnetite to granule-shaped clusters of minute opaque inclusions within fayalite but those present in the western parts of the unit consist of finely disseminated magnetite in a matrix of acicular cummingtonite. Many transi-

tional types of relic magnetite-rich granules occur in the intervening area. Quartzose granules are also common except in the thoroughly recrystallized eulysites.

*Submember N.*—This silicate-rich quartzose unit is normally only 3 to 5 feet thick but because of its negligible magnetite content it normally forms a rather distinct horizon except in some of the westernmost holes. The unit was recognized in all but two of the western drill holes.

Most of the material of unit N consists of quartz with minor to locally abundant amounts of silicates. Most of the core from holes east of Iron Lake has recognizable amounts of fayalite, and some ferrohypersthene, in a quartzose matrix that locally contains some fine-grained cummingtonite. West of hole 25, fine-grained cummingtonite is locally abundant in the quartzose taconite. Minute remnants of fayalite, however, are apparent in many of the thin sections of these specimens. Only a few thin magnetite layers (up to about $\frac{1}{4}$ inch thick) or thin layered zones (up to near 1 inch thick) are ever present in the unit. Many quartzose granule structures are apparent in the western holes.

*Submember M.*—In contrast to other submembers of the Upper Cherty member, the magnetite layers of unit M, in general, are relatively thin and well-bedded. This submember generally ranges from 15 to 25 feet in thickness and is somewhat thinner in the western part of the area. Most of the individual magnetite-rich layers are less than $\frac{1}{4}$ inch thick but some groups of closely-spaced magnetite lamellae form layers up to $\frac{1}{2}$ inch thick. In most core, thin magnetite-rich and thin quartz-silicate-rich layers are interbedded to form several thicker, layered zones 2 to 6 inches, rarely 12 inches, thick.

The quartzose layers that separate the magnetite-rich layers are generally about 2 to 4 inches thick. The cores from holes 18, 19, 20 and those farther to the east commonly contain moderate amounts of fayalite, especially in the quartzose layers. Some cores contain minor amounts of hedenbergite. Except locally, fine-grained cummingtonite is virtually absent. Proceeding westward, from the region south of Argo and Iron lakes, decreasingly small remnants of fayalite and some ferrohypersthene, within increasing amounts of fine-grained cummingtonite, are present in quartzose layers. Core from hole 30 marks the westernmost occurrence of fayalite. In the remaining holes, fine-grained cummingtonite is locally abundant but generally decreases slightly in amount to the west. Magnetite-rich granule structures are common in core from holes west of Iron Lake.

*Submember L.*—For the purposes of discussion of submembers L and K only, holes numbered from 4 to 20 are called the eastern holes. Unit L is similar in many aspects to the adjacent units. Although slightly pebbly throughout it is generally somewhat less conglomeratic than unit K above whereas unit M below is distinctly less pebbly. For the majority of the western holes, it is generally true that the upper part of the unit consists mostly of relatively abundant, thin, magnetite-rich layers and the bottom part mainly of densely packed-magnetite-rich granules. In most of the eastern holes, the transition from abundant thin magnetite layers to the abundant magnetite-rich granules is not as apparent as in the western holes. Unit L

averages about 15 feet thick in the east to about 45 feet in the west and is 46 feet thick near Mesaba.

Almost all of the individual magnetite-rich layers are less than $\frac{1}{4}$ inch thick and they are both regularly and irregularly bedded. Most of the magnetite in this unit occurs as many closely spaced thin layers that collectively form relatively rich layered zones ranging from $\frac{1}{4}$ to 6 inches, rarely to 12 inches, but mostly between 2 and 3 inches thick.

The interbedded, silicate-bearing, quartzose layers, both within the eastern and western holes, are slightly lenticular and range from $\frac{1}{4}$ to 8 inches but most are between 2 to 4 inches in thickness. Although magnetite-rich granules are present throughout most of the quartzose layers of the unit, granules become increasingly apparent and abundant with depth. Complete recrystallization in the eastern area has destroyed almost all of the granule structures, assuming they were once present as abundantly as elsewhere.

Ferrohypersthene is commonly abundant in the magnetite-rich beds of the core from the eastern holes and moderate amounts also appear locally in the quartzose layers, especially as coarse-grained porphyroblasts up to 4 cm diameter. Hornblende and some hedenbergite are also locally abundant in most of these cores whereas only minor amounts of actinolite, and even less cummingtonite, occur.

In the core from the western holes, abundant fine-grained cummingtonite and minor amounts of actinolite occur in the magnetite-rich beds and the quartzose layers. Minor amounts of calcite are associated with cummingtonite in a few of these cores. A few coarse-grained porphyroblasts of hedenbergite and ferrohypersthene occur in some places. The presence of a great variety of relic granule structures, mainly outlined by fine-grained magnetite, is generally characteristic of the quartzose layers of the cores from this area.

*Submember K.*—Submember K is heterogeneous with respect to the variety of rock types that compose the unit. Generally, it is also somewhat conglomeratic and pebbly throughout and the quartzose layers usually have a distinct granule texture. Magnetite-rich layers are plentiful but show a wide variation in perfection of bedding and of association with the many silicates present. In a very general way, the magnetite-rich layers and the interbedded quartzose layers are thin and closely spaced near the top of the unit and are usually somewhat thicker and more widely spaced near the bottom. Again for the purposes of discussion of this unit, holes numbered from 4 to 20 are referred to as the eastern holes. Unit K increases irregularly from an average thickness of 30 feet in the eastern holes to about 40 feet in the western holes. It is about 48 feet thick near Mesaba.

Magnetite-rich layers occur in two ways and both appear to be equally abundant and distributed throughout the unit. In one case, magnetite occurs in thin layers up to about $\frac{3}{4}$ inch thick. These individual layers are generally lenticular or irregularly bedded and they commonly diverge into a series of thinner or thicker magnetite beds that are separated by a few thin lenticular quartzose- or silicate-rich lamellae. The other occurrence consists of an interbedded sequence of thin magnetite-rich layers, of the type just described,

and quartzose- and silicate-rich layers of similar thickness. These zones of abundant magnetite-rich layers range in thickness from ¼ to 8 inches but most are from 1 to 3 inches.

The quartzose and silicate-rich quartzose layers separating the magnetite-rich parts of the rock in both the eastern and western holes are generally somewhat lenticular. These layers range in thickness from ⅛ to 9 inches but most of them are between 1 and 4 inches. The quartzose layers commonly contain many magnetite-rich pebbles, apparently of intraformational conglomeratic origin. Magnetite-rich granules are abundant in the quartzose layers of the core from the western holes. They are somewhat obscure in core from holes that contain abundant silicates as well as in the highly recrystallized core from the eastern holes.

Actinolite and usually lesser amounts of cummingtonite are locally abundant within and adjacent to the magnetite-rich parts of nearly all the core from the eastern holes. Only minor amounts of these amphiboles are present in the quartzose layers except next to the magnetite-rich layers.

Fine-grained cummingtonite and lesser amounts of actinolite are typically abundant in the magnetite-rich zones in core from the western holes. The quartzose layers generally contain moderate to locally abundant amounts of fine-grained cummingtonite. A few occurrences of coarse-grained hedenbergite and ferrohypersthene in the quartzose layers were noted in core from the western holes. Actinolite is not common within the quartzose layers except where associated with the pyroxenes.

*Submember J.*—In the discussion of the remaining submembers of the formation, holes numbered from 25 to 37 are again considered as the western holes. Submember J contains a highly mixed variety of relic sedimentary structures. In the core from the western holes and holes 18 and 21, the unit could even be further subdivided into three more or less distinct subunits. In these cores, the bottom parts of the unit contain abundant lenticular and slightly irregularly-bedded magnetite-rich layers averaging about ½ inch thick. The middle portion is characterized by the almost ubiquitous magnetite-rich pebbles and somewhat coarse fragments of intraformational conglomerates. The upper part typically contains abundant closely-packed magnetite-rich granules. This characteristic distribution is not present in the core from the eastern holes. In contrast, there the entire unit contains mainly granules and pebbles throughout and the presence of lenticular, conglomeratic and brecciated strata is common. The unit averages about 17 feet thick. Only the uppermost subunit of J could be recognized in core from near Mesaba, where the thickness of the entire unit is 22 feet.

The matrix in which the magnetite is distributed is distinctly quartzose everywhere. Moderate amounts of hedenbergite and some ferrohypersthene are locally present in core from the whole area but especially from the eastern holes. The most coarse-grained occurrences of these pyroxenes, in stubby prisms up to 5 mm long, are in core from hole 36. Cummingtonite is absent in core from the eastern holes but locally occurs to a minor extent in some of the western drill core. A few grains of fayalite are present in core from

holes 19 and 21. A rare occurrence of reibeckite was found in core from hole 28.

*Submember I.*—This unit is defined by the presence of algal structures. It is generally about 5 feet thick but is only about 3 feet thick near Mesaba. Grout and Broderick (3, p. 21) were among the first to recognize the organic origin of these structures. Although some algal colonies are recovered intact in the core, more commonly only conglomeratic zones containing fragments of the algal structures are found. The intraformational conglomeratic nature of the unit is persistent throughout the area. Some relic bedding, mostly as indistinctly bedded lamellae, occurs locally with the conglomerates.

The algal structures, as well as the many granule structures, are delineated by the distribution of fine-grained magnetite within fine-grained quartz. Most of the minerals forming the delicate algal structures have been partially recrystallized. In core from the region south and west of Iron Lake, martite has subsequently developed. Many of the fine-grained granules and delicately preserved algal structures of this area also contain hematite, essentially as dust sized particles, which may or may not be martite. Martite and dusty hematite is almost invariably associated with minute amounts of calcite, and in many places actinolite; rarely with muscovite and riebeckite. Cummingtonite is virtually absent from this unit, except for minor amounts in core from hole 29, and minor amounts of andradite, clinohypersthene and hedenbergite are locally present in some cores from holes southwest of Iron Lake.

*Submember H.*—This submember is characterized, in part, by the presence of greenish silicate assemblages occurring as thin, muddy-looking layers within the magnetite-rich layered zones of the unit. Most of the drill holes of the area cut the unit, which averages about 8 feet thick in the western holes and gradually increases to an average of about 12 feet in the easternmost holes. The core from the hole near Mesaba that has been correlated with unit H, however, is nearly 30 feet thick.

Fine-grained magnetite occurs in slightly irregularly-bedded to lenticular lamellae and thin layers up to $\frac{1}{4}$ inch thick. These thin beds commonly form a group of closely spaced layers that are typically interlayered with, and enveloped by, actinolite- and hornblende-rich layers of similar thickness. These layered zones of magnetite- and silicate-rich beds range from $\frac{1}{2}$ to 6 inches thick, but are mainly about 2 to 3 inches thick. In a few holes, minor amounts of cummingtonite associated with actinolite or hornblende have produced a silicate assemblage of a yellowish green color.

The magnetite-silicate layered zones are interbedded with quartzose beds that range from about $\frac{1}{2}$ to 6 inches thick. These beds are commonly slightly thicker, mostly between 1 and 4 inches, than the interlayered magnetite- and silicate-rich zones. Except in some of the core from the eastern holes, the granule nature of the quartzose layers is usually evident. Minor amounts of hedenbergite occur in the quartzose layers of core from most holes and minor amounts of fayalite are also present in core from some eastern holes.

### *Upper Slaty Member*

The entire Upper Slaty member was cut completely by only four drill holes, 18, 21, 25 and 32, and almost completely by hole 34. It shows a uniform thickness of about 125 feet. The cores from most holes, and the hole near Mesaba, contain some of the lower units of the member. The Upper Slaty member has been divided into seven submembers: A, B, C, D, E, F and G.

This member typically contains interbedded zones consisting of magnetite- and silicate-rich lamellae in many places. A large part of the rock, however, consists of thin quartzose layers that contain many granule structures. Mineralogically and texturally it is strikingly similar to many parts of the Upper Cherty member except that it contains more silicate-rich lamellae and also that the individual magnetite and quartzose layers of the Upper Cherty member are typically thicker.

In passing from the Upper Cherty member into the Upper Slaty member, there is generally a gradational increase in the well-bedded nature of the Slaty member because its lamellae become more regularly bedded and the layered zones themselves become more uniformly layered and abundant.

*Submember G.*—The presence of andradite is locally characteristic in core of unit G from many drill holes throughout the area. In general, the unit contains many thin, laminated, magnetite-rich zones but in comparison to other submembers of the Upper Slaty member, these zones are not abundant. An average thickness of 25 feet was determined in the core from about 20 holes. Units F and G, whose composite thickness is 50 feet, could not be differentiated in core from the hole near Mesaba. The basal parts of the core from several drill holes from south and east of Argo Lake consists of rock types identical to those occurring in the overlying unit H and are not discussed further. During mapping, this basal unit was termed G′. It ranges in thickness from about 20 feet in core from hole 6 to about 9 feet in core from hole 22.

Closely spaced, magnetite-rich lamellae commonly form thin layered zones mostly ranging in thickness between 1 and 6 inches, with zones 1 to 3 inches most common. The individual lamellae and laminated zones are more irregularly bedded, less sharply defined and did not accumulate to the moderate thicknesses of the layered zones of the overlying unit. In the core from these western holes, very poorly layered, densely packed zones of magnetite-rich granules instead of lamellae are more abundant. These irregular, presumably lenticular to tabular zones of abundant granules generally range in thickness from $\frac{1}{2}$ to 8 inches, the most of which are about 2 to 3 inches or less.

Moderate amounts of actinolite have locally developed within and adjacent to the magnetite-rich granule and laminated zones in core from most of the holes. As a rule, however, the material within and between the magnetite-rich granule and laminated zones is quartzose. No cummingtonite is present in core from holes farther east than hole 20 but minor amounts are found in a few cores from some of the remaining holes.

The relatively magnetite-rich zones are separated by fine-grained

quartzose layers. Although the quartzose layers range from ½ to 12 inches, almost all are between 1 to 8 inches thick. The granule nature of this lean quartzose material is rather obscure in the slightly more recrystallized core from holes east of 21. Abundant magnetite-rich granule structures become increasingly apparent in core of hole 21 and holes farther west.

Andradite commonly occurs in the quartzose parts of many cores and is the most characteristic mineral of unit G. Its abundance and occurrence has an unexpected lateral variation. Only minor to moderate amounts of andradite occur in most of the eastern holes, and even core from a few holes like 18 and 21 contain no garnet. Garnet, however, is locally abundant in the core from the remaining holes extending from hole 24 to 34; all of which are much farther from the present gabbro contact. Minor amounts of hedenbergite and lesser amounts of diopside also occur in the quartzose layers of core from throughout the area and in many places they are associated with andradite.

*Submember F.*—Submember F is characterized by relatively thick zones of regularly bedded, alternating lamellae of magnetite and cummingtonite, which are separated by quartzose layers that generally have a granule texture. This unit is persistent and is recognized readily in most core but it could not be differentiated in core from some far eastern holes and the hole from near Mesaba. Unit F averages approximately 15 feet thick in the eastern holes and about 24 feet thick in the western holes.

Alternating lamellae consisting mainly of fine-grained magnetite and fine-grained quartz and cummingtonite, of slightly differing thickness, collectively form the thick laminated zones of the unit. Most of the individual lamellae are from $\frac{1}{16}$ to ¼ inch thick and are, as a rule, regularly bedded and uniform. Almost all of these laminated zones range in thickness from about ½ to 8 inches but most are 2 to 6 inches thick. From hole 20 westward, the typically fine-grained, acicular to prismatic cummingtonite becomes more pronounced. Most of the cummingtonite, and rarely actinolite, occurs in the lamellae that are interlayered with magnetite.

The degree of excellence of the primary layering of unit F makes it ideal for the preservation of relic sedimentary bedding structures. Many examples of penecontemporaneous slumping, folding and faulting of the laminated zones are present. Apparently many of the original layers attained a sufficient degree of competence to be distorted and brecciated without being completely destroyed. Grout and Broderick (3, p. 23) and Broderick (1, p. 450) have interpreted these structures as drag folds. The writer, however, believes these structures are of primary sedimentary origin because the delicate lamellae above and below are essentially undisturbed and the "fold" and "breccia" structures are truncated in many places by thin and delicate, undisturbed lamellae. All degrees of disruption from a slightly folded sequence of these laminated zones to well formed intraformational or edgewise conglomerates of laminated zone fragments were observed.

The thick, laminated magnetite-cummingtonite zones are separated by quartzose layers that commonly have granule structures outlined by fine-grained magnetite. The quartzose layers range from ½ to 12 inches in

thickness but most are ½ to 6 inches, and the average is about 2 to 3 inches. In comparison to the laminated zones, only minor amounts of cummingtonite occur in quartzose layers. Numerous small pods and irregular masses of andradite, at places accompanied by minor amounts of hedenbergite, were noted in the quartzose layers of core from several holes.

*Submember E.*—This generally massive quartzose unit contains distinctly fewer magnetite-bearing laminated zones than the adjacent units. It is characterized by the local presence of septaria structures, and by abundant magnetite-bearing granules. It was encountered in many drill cores and has an average thickness of about 6 feet. The unit was not recognized in the core from the hole near Mesaba.

Most of the magnetite-rich laminated zones are poorly bedded and are less than ½ inch thick. Closely associated with these zones are thin beds of similar thickness that contain abundant granule-shaped clusters of small magnetite grains. Both magnetite-rich lamellae and granules are commonly combined to form thicker, relatively magnetite-rich zones that vary between ½ and 6 inches but most of which are 1 to 3 inches thick. Thin layers, up to ½ inch thick, of fine-grained cummingtonite and lesser amounts of actinolite are almost invariably associated with, and are locally abundant within, these magnetite-rich zones.

The non-laminated beds forming most of the unit normally consist of fine-grained quartzose layers that have a distinct granule fabric. Most of the quartzose layers are 2 to 4 inches thick but may vary from ¼ to 6 inches.

Septaria-like structures, consisting of whitish, quartz-filled "fractures" that occur within the granule-bearing quartzose layers, were found in core only from holes 30 and 32. The fact that a few such structures were encountered, although rare, does support the tentative correlation of submember E with part of the septaria-bearing unit recognized by Grout and Broderick (3, p. 17).

*Submember D.*—Most of the magnetite-rich laminated zones of unit D are uniformly thick to slightly lenticular and thereby somewhat resemble the overlying unit C. Unit D, however, is characterized by the presence of very lenticular layers to nearly pebble-shaped lenses of whitish fine-grained quartzose material between the magnetite-rich laminated zones. Unit D averages about 7 feet in the core from the Eastern Mesabi. The uppermost 20 feet of core from the hole near Mesaba are from this unit.

Numerous magnetite-rich lamellae form laminated zones from ¼ to 3 inches thick but most of which are about ½ to 1 inch. Almost without exception, these laminated magnetite zones are associated with fine-grained amphiboles. Actinolite is generally abundant in most of the core specimens but cummingtonite is also locally abundant, especially from some holes to the southwest of Iron Lake.

Most of the chert-like quartzose layers that separate the laminated magnetite zones are distinctly lenticular and range from ¼ to 3 inches in thickness, with layers from ¼ to 1 inches being most common. Many of these layers are distinctly in the form of small roundish pods or lenses, commonly about an inch or less in diameter. In comparison to all the quartzose layers of the other submembers of the Upper Slaty member, these lenticular quartzose

layers are strikingly devoid of obvious granule structures. Relics of granules, nevertheless, are apparent in thin section. Locally moderate amounts of hedenbergite are present in the quartzose layers of core from holes 18, 21, 30, and 32; minor amounts of andradite also appear with the pyroxene in core from the last hole.

*Submember C.*—Submember C is the uppermost unit of the iron formation containing considerable magnetite and generally consists of laminated zones that are separated by uniform quartzose layers. The average thickness is about 42 feet as determined from the core of eight drill holes.

The distinctly laminated portions typically consist of slightly irregularly- to regularly-bedded, magnetite-rich lamellae within a quartzose or silicate matrix. These lamellae are present singly and as closely spaced groups constituting uniform, laminated zones up to $\frac{1}{2}$ inch thick that are separated by fine-grained quartzose layers most of which are $\frac{1}{4}$ to 1 inch thick. A few quartzose layers as thin as $\frac{1}{16}$ inch or as thick as 5 inches are present, however, in most core. Almost all of the quartzose layers show no obvious granule structures in hand specimen or thin section. In many places, the quartzose layers are vaguely laminated with extremely fine-grained magnetite and thin sections of these layers show excellent relic textures of bedded chert. Minor amounts of hedenbergite are commonly found in the quartzose layers of the unit. Medium-grained ferrohypersthene, along with minor fayalite, is common in and surrounding the magnetite-rich laminated zones in core from the eastern holes. Minor amounts of fayalite occur alone in core from hole 32. Cummingtonite is locally abundant in both the magnetite-rich and quartzose layers of the unit everywhere and in many places is associated with minor amounts of actinolite and hornblende.

*Submember B.*—This unit consists almost entirely of irregular layer-like masses of pyroxenes and amphiboles, averaging 1 to 2 inches thick, that have developed within vaguely-bedded chert-like quartzose layers. As a whole, it is indistinctly bedded and is essentially devoid of magnetite, except for a few lamellae near the bottom of the unit. Specimens of the submember were obtained only in four drill holes from which the average thickness of the unit is found to be 16 feet.

Normally a light green diopside is most abundant but lesser amounts of darker green hedenbergite are generally also present in most cores. Both pyroxenes are mostly medium grained and granoblastic in texture but many subhedral prisms of each are over 5 mm long in some places. Some small irregular masses of coarse-grained hornblende, with minor amounts of apatite and stilpnomelane, are found in a few cores. Some cores also contain minor amounts of cummingtonite as crude layer-like patches $\frac{1}{2}$ to 2 inches thick within the pyroxene-rich zones. Several trace occurrences of chalcopyrite and pyrrhotite were found in three of the holes.

The chert-like quartzose layers are poorly- to indistinctly-laminated and are commonly $\frac{1}{4}$ and 1 inch thick. The relic laminations are best preserved in the most fine-grained layers because slight local recrystallization has partially destroyed many lamellae elsewhere. The pyroxenes are virtually absent from the quartzose layers but minor amounts of cummingtonite,

actinolite and minute amounts of stilpnomelane locally enhance the laminated aspect of the layers.

*Submember A.*—This submember is the uppermost stratigraphic unit of the Biwabik iron-formation. It is a calcite marble and as such is easily distinguished from the apparently conformable, overlying Virginia formation. Specimens of this unit occur in the core from only four holes in which the thickness of the unit averaged about 5 feet.

On the Eastern Mesabi range, this lime-silicate bearing marble is nearly white to light bluish-gray in core from hole 32 but is medium gray to gray-black in core from the other holes farther east. The only apparent difference between the light and darker varieties of marble is the relative abundance of unidentified minute black specks, probably graphite, occurring as inclusions within and surrounding the calcite grains.

Most of the silicates occurring in the cores are too fine-grained to be readily identified with the hand lens. Thin sections of this material indicate a dominance of diopside, which in several places gives the marble a greenish cast. Minor amounts of medium-grained idocrase and andradite, however, are easily recognized in core from hole 21. Likewise, some andradite and locally abundant amounts of coarse-grained wollastonite and diopside are present in core from hole 32.

## Virginia Formation

The area underlain by the Virginia formation in the Eastern Mesabi district consists of a swamp-like depression. There are no outcrops of the formation near the current mining operations but some occur to the west. Specimens of the formation were found in core from several holes both near and far from the gabbro. The metamorphism of the Virginia formation by the Duluth gabbro and diabase sills will be discussed in another paper.

Briefly, the greater part of the Virginia formation may be best described as a slightly metamorphosed, light gray, somewhat laminated, quartz graywacke; now a fine-grained quartzose hornfels. For many core specimens, a binocular microscope is required to distinguish the metamorphosed formation from some of the fine-grained varieties of diabase sills that locally occur within it.

Within a few hundred feet of the present gabbro contact, as in core from holes 2 and 3, the formation has been completely recrystallized to a medium- to fine-grained quartz-biotite-anorthoclase (orthoclase?) hornfels. Although the concentration of biotite into lamellae probably reflects initial lamination, these layers are not foliated but typically have a decussate fabric. Minute amounts of interstitial pyrrhotite are present locally. Core from hole 2, drilled after the present study was essentially completed, in addition, contains trace amounts of wollastonite, diopside and iron-rich cordierite, most of which has altered to a very pale green chlorite-like material resembling prasiolite.

About 4,000 feet from the contact, in core from hole 21, the recrystallization has produced a fine-grained chlorite-white mica (muscovite?) quartz-orthoclase hornfels. Biotite is present in trace amounts only. In general, the minerals are more clouded by inclusions than those in the specimens nearer

the gabbro. A thin, impure carbonate-rich zone within the Virginia formation from this hole has recrystallized to yield a complex lime-silicate calcite marble, which consists of an interlocked mosaic of calcite grains that are dusty with many minute unidentified inclusions. These inclusions are presumed to be mineralogically the same as the larger grains of diopside, idocrase, sphene, periclase and leucoxene that occur interstitially.

It is easy to see in a thin section from hole 25, almost two miles from the present gabbro contact, that some parts of the Virginia formation were originally immature quartz graywackes. The angular or "grity" fabric of the quartz grains and a few altered (sericitic?) fragments of feldspar are still evident. The enclosing fine-grained matrix material is typically cloudy and consists mainly of slightly recrystallized grains of quartz, white mica (muscovite or sericite) and some biotite, chlorite and orthoclase (?, a silicic feldspar of negative relief).

### Diabase Dikes and Sills

Small diabase sills are present in several holes of the eastern area and one was cut by hole 32. Diabase dikes also occur in the Mitchell pit near 6,600 feet west along the pit baseline and in a small drainage ditch east of the pit.

The diabases are generally dark gray and fine grained and as such are somewhat similar in appearance to the metamorphosed Virginia formation. Core specimens indicate that the sills range from about one to 15 feet in thickness. They characteristically occur in the upper part of the Upper Slaty member or near the bottom of the Virginia formation. The dikes observed in the pit range up to 35 feet in width.

There is no evidence of metamorphism of the iron formation by the diabase intrusives because both rocks have been subsequently highly metamorphosed. A fine-grained diabasic fabric is still relic in most specimens but thin sections show resorbed remnants of plagioclase laths and the typical tendency to form a hornfelsic fabric among the augite and plagioclase grains.

### Duluth Gabbro

No fresh exposures of the Duluth gabbro occur near the present pit operations and the gabbro-iron formation contact is concealed. Coarsely recrystallized parts of the iron formation exposed at the eastern end of the Mitchell pit, however, probably lie within 500 feet horizontally of the gabbro. Fresh (artificial) exposures of the gabbro are available in the ore conveyor tunnel at the base of the crusher pit, a few hundred yards south of hole 1. Core from holes 1 and a number of shallow holes from the crusher site provided many gabbro specimens.

In hand specimen, this rock is a light to dark green gabbro that shows a variety of textures ranging from xenomorphic granular to diabasic to trachytoid and locally shows a "banded" (pseudo-layered) or stratiform structure. Plagioclase typically occurs as lath-like, subhedral grains and both olivine and augite generally occur interstitially as fine-grained anhedra. Minor amounts of chalcopyrite and pyrrhotite are locally abundant in a few core specimens. In several places, it appears that the sulfides have com-

pletely replaced olivine or augite while still preserving a fair diabasic fabric of the plagioclase laths. The sulfides are characteristically associated with the mafic minerals particularly coarse-grained biotite, both of which locally appear to have been deuteric or post-magmatic.

In thin section, most of the specimens may be classified as olivine gabbro but some parts of the complex are either simple gabbros or troctolites. The plagioclase is labradorite ($An_{60}$), which possesses incipiently developed spindle-shaped pericline? twins that somewhat complicate the dominant albite twinning. A few grains are faintly zoned (normal) with slightly less calcic rims but this is not a common feature. A few anhedra of quartz interstitial to plagioclase are present but are rare.

Olivine anhedra normally occur interstitially to the plagioclase to form a hypautomorphic granular rock with a coarse-grained diabasic fabric. In many places, the olivine grains have thin coronas of augite (Ti-rich?). Augite also occurs interstitially to plagioclase in a fashion similar to olivine. In some places, however, it poikilitically encloses olivine and less commonly plagioclase to produce an ophitic fabric.

Brown biotite obviously appears to have been one of the last silicates to form. In many places it is not clear if it was a late-stage magmatic mineral or is a product of a later high-temperature alteration. Its association with highly altered feldspars, abundant apatite, replacement sulfides and recrystallized parts of the gabbro support the latter view. In many places, fine-grained biotite commonly surrounds or rims the mafic minerals or the minor amounts of accessory magnetite present and appears as if it might have been a late magmatic mineral.

With the exception of the sulfides and magnetite, all of the above minerals have been affected or altered by later, probably aqueous, solutions. Olivine, especially is commonly altered to a brownish nontronite- or hisingerite-like mineral and to a lesser extent by a pale greenish mineral resembling bowlingite.

MINES EXPERIMENT STATION,
UNIVERSITY OF MINNESOTA,
MINNEAPOIS 14, MINNESOTA,
*September 12, 1959*

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# THE CONSTITUTION OF DAVIDITE[1]

J. D. HAYTON

ABSTRACT

Analyses are presented of samples of davidite from South Australia and South Africa. Brief reference is made to methods of analysis with comments on the states of oxidation of the components. A basis is suggested for determining the constitution of davidite and several possibilities are discussed. It is concluded that davidite is homogeneous in nature and not heterogeneous as suggested by A. W. G. Whittle (1) in a paper of this title.

## INTRODUCTION

DURING the past ten years samples of davidite have been obtained that were reasonably free from impurities. The samples came from Radium Hill and Mount Pleasant in South Australia as described by Whittle, (1) from a new locality at Kalabity homestead, 30 miles NNW of Radium Hill and also from Tete, Mozambique, Africa.

The samples were prepared by preliminary hand selection under a binocular microscope followed by heavy liquid separation of minus 60 mesh material. Some of the samples were further treated in a "Frantz" Isodynamic Separator. The final product was examined for foreign material by preparing polished sections of representative portions mounted in bakelite briquettes. Small amounts of impurities were present, mostly as intergrowths or exsolution bodies. They consisted mainly of rutile, hematite, ilmenite, and quartz and in most instances the amounts detected optically did not exceed 5 percent of the davidite. No allowance was made for impurities other than rutile and silica when calculating the probable combinations of components in the davidite.

## METHODS OF ANALYSIS

Most of the components were determined by well known procedures that were modified as required. The lanthanons,[2] thorium, lead, and alkaline earths were separated as insoluble fluorides by a preliminary treatment with hydrofluoric acid; uranium was also precipitated as uranous fluoride at this stage unless an oxidizing acid ($HNO_3$) were present. The purified lanthanon oxides, which also contained the thoria, were examined spectrographically to determine the relative amounts of the individuals.

Some of the components were determined directly in the davidite by X-ray fluorescence analysis and by spectrographic analysis. The results

[1] Published with the approval of the Director of Mines and Government Geologist, Adelaide, S. A.

[2] In this paper "lanthanons" refers to the elements Lanthanum to Lutecium inclusive in the periodic table. The symbol Ln is used to denote lanthanons and the oxides are represented by $Ln_2O_3$.

TABLE 1

PROBABLE CORRECTION OF MEASURED FeO FOR VARIOUS VALENCE STATES OF U, V

| Davidite No. | Oxidation states | | | | |
|---|---|---|---|---|---|
| | U(IV) V(V) | U(IV) V(III) | U(VI) V(V) | U(VI) V(IV) | U(VI) V(III) |
| 1 | +1.2 | −1.6 | $\frac{+4.6}{+1.2}$ = 5.8 | +4.6 | $\frac{+4.6}{-1.6}$ = 3.0 |
| 2 | +1.0 | −1.3 | $\frac{+4.6}{+1.0}$ = 5.6 | +4.6 | $\frac{+4.6}{-1.3}$ = 3.3 |
| 4 | +1.4 | −1.8 | $\frac{+3.6}{+1.4}$ = 5.0 | +3.6 | $\frac{+3.6}{-1.8}$ = 1.8 |
| 5 | +1.2 | −1.5 | $\frac{+4.3}{+1.2}$ = 5.5 | +4.3 | $\frac{+4.3}{-1.5}$ = 2.8 |
| 6 | +1.6 | −2.0 | $\frac{+2.3}{+1.6}$ = 3.9 | +2.3 | $\frac{+2.3}{-2.0}$ = 0.3 |
| 7 | +0.3 | −0.4 | $\frac{+1.1}{+0.3}$ = 1.4 | +1.1 | $\frac{+1.1}{-0.4}$ = 0.7 |
| 8 | +0.1 | −0.1 | $\frac{+0.7}{+0.1}$ = 0.8 | +0.7 | $\frac{+0.7}{-0.1}$ = 0.6 |
| 9 | +0.15 | −0.2 | $\frac{+0.7}{+0.1}$ = 0.8 | +0.7 | $\frac{+0.7}{-0.2}$ = 0.5 |
| 10 | +0.3 | −0.4 | $\frac{+3.8}{+0.3}$ = 4.1 | +3.8 | $\frac{+3.8}{-0.4}$ = 3.4 |
| 11 | +2.0 | −2.9 | $\frac{+2.4}{+2.0}$ = 4.4 | +2.4 | $\frac{+2.4}{-2.9}$ = − 0.5 |

obtained for uranium, lead, and thorium agreed reasonably well with results of chemical analysis.

*Ferrous Iron Determination.*—The method proposed by Wilson (2) was used for determining the apparent amounts of ferrous iron, but the figures

TABLE 2

| Davidite No. | FeO determined % | Max. + Ve correction % | Max. possible FeO % | Max. − Ve correction % | Min. possible FeO % |
|---|---|---|---|---|---|
| 1 | 12.0 | 5.8 | 17.8 | 1.6 | 10.4 |
| 2 | 17.4 | 5.6 | 23.0 | 1.3 | 16.1 |
| 4 | 10.3 | 5.0 | 15.3 | 1.8 | 8.5 |
| 5 | 6.1 | 5.5 | 11.6 | 1.5 | 4.6 |
| 6 | 13.2 | 3.9 | 17.1 | 2.0 | 11.2 |
| 7 | 13.5 | 1.4 | 14.9 | 0.4 | 13.1 |
| 8 | 19.4 | 0.8 | 20.2 | 0.1 | 19.3 |
| 9 | 14.9 | 0.8 | 15.7 | 0.2 | 14.7 |
| 10 | 16.2 | 4.1 | 20.3 | 0.4 | 15.8 |
| 11 | 21.6 | 4.4 | 26.0 | 2.9 | 18.7 |

obtained could not be accepted as correct except in davidites with low uranium and vanadium contents, since the actual state of oxidation of those components is uncertain.

The effect of other components on the apparent ferrous iron content can be calculated from consideration of the probable reactions when davidite is dissolved in dilute hydrofluoric acid. Under these conditions, ferric ions are complexed and the redox value of the system, $Fe^{3+}/Fe^{2+}$ is lowered sufficiently for $UO_2^{++}$ to be reduced to $U^{4+}$ with subsequent precipitation of $UF_4$. The reactions likely to occur for various oxidation states of U and V are given below, the components being expressed as their corresponding oxides.

$$\underset{286}{UO_3} + \underset{144}{2FeO} \rightarrow UO_2 + Fe_2O_3 \qquad (1)$$

$$\underset{182}{V_2O_5} + \underset{144}{2FeO} \rightarrow 2VO_2 + Fe_2O_3 \qquad (2)$$

$$\underset{150}{V_2O_3} + \underset{144}{Fe_2O_3} \rightarrow 2VO_2 + 2FeO \qquad (3)$$

Hence—if (1) occurs, the measured FeO should be increased by an amount equal to $\left(\frac{144}{286}\right)$ or one half of the uranium expressed as $UO_3$.

If (2) occurs, the FeO should be increased by $\left(\frac{144}{182}\right)$ or seven ninths of the vanadium expressed as $V_2O_5$.

If (3) occurs, the FeO should be decreased by the vandium expressed as $V_2O_3$.

It is considered that no reaction is likely if both uranium and vanadium exist in the quadrivalent condition. The calculated effects of U and V for the various davidites are shown in Table 1.

Table 2 shows FeO determined by the method of Wilson (2) together with the estimated maximum possible differences between the measured and true values.

The possible variations are considerable except in number 7, 8 and 9, where the estimated difference from the measured value does not exceed 1.4 percent and in 8 and 9 is less than 1 percent. In number 11, positive corrections are not applicable since the total iron expressed as FeO is actually less than the determined value for FeO, the respective figures being:

| | |
|---|---|
| Total Fe as FeO | 21.2 percent |
| FeO as determined | 21.6 percent |

If it is assumed in this case that uranium is quadrivalent and vanadium trivalent, then the difference between the total iron and corrected ferrous iron would represent the amount of ferric iron present in the davidite, hence—

| | |
|---|---|
| Total Fe as FeO | 21.2 percent |
| Corrected FeO | 18.7 percent (Table 2) |
| Remainder as FeO | 2.5 percent |
| Ferric oxide | 2.7 percent |

## RESULTS

Descriptions of the samples and results of the analyses are given in Table 3.

It is of interest that the Mozambique analyses numbers 1 and 2 are practically identical except for the apparent FeO value (Table 2). These samples were originally selected because of their markedly dissimilar physical character, number 1 being like chromite in appearance while number 2 exhibited the typical vitreous lustre and conchoidal fracture of rare earth minerals. The difference in physical appearance may be related to the difference in apparent FeO content although there was no similar feature

TABLE 3

ANALYSES OF DAVIDITE FROM MOZAMBIQUE AND SOUTH AUSTRALIA

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $TiO_2$ | 47.4 | 46.8 | 54.5 | 44.9 | 46.3 | 47.7 | 50.1 | 53.1 | 52.7 | 48.5 | 42.6 |
| FeO | 26.1 | 26.1 | 16.5 | 30.1 | 30.8 | 27.8 | 13.5 | 19.4 | 14.9 | 29.4 | 18.7 |
| $Fe_2O_3$ | | | 10.2 | | | | 13.4 | 7.3 | 12.2 | | 2.7 |
| $Cr_2O_3$ | 4.3 | 4.8 | 0.17 | 0.2 | 0.6 | 0.6 | 1.3 | 0.1 | trace | 0.3 | 1.2 |
| $V_2O_5$ | 1.6 | 1.3 | 1.4 | 1.8 | 1.5 | 2.0 | 0.4 | 0.1 | 0.2 | 0.4 | 3.5 |
| Undetermined[a] | 2.2 | 1.8 | — | 2.4 | 0.5 | 1.4 | 2.2 | 2.6 | 1.6 | 1.7 | 3.5 |
| MnO | trace | trace | — | 0.05 | — | 0.1 | — | 0.3 | — | — | 0.2 |
| $UO_3$ | 9.2 | 9.2 | 9.8 | 7.2 | 8.7 | 4.6 | 2.2 | 1.5 | 1.5 | 7.6 | 4.8 |
| PbO | 0.8 | 0.8 | 0.72 | 0.9 | 0.9 | 0.7 | 0.6 | 0.3 | 0.3 | 0.5 | 1.2 |
| $Sc_2O_3$[d] | 0.2 | 0.2 | n.d. | 0.2 | 0.2 | 0.3 | 0.3 | 0.1 | 0.03 | 0.03 | 0.2 |
| $ThO_2$[c] | 0.4 | 0.4 | 0.07 | 0.3 | 0.2 | 0.3 | 0.4 | 0.4 | 0.4 | 0.4 | 0.2 |
| $Ln_2O_3$[b] | 5.7 | 5.8 | 5.6 | 7.2 | 6.1 | 9.8 | 9.4 | 9.6 | 10.2 | 7.0 | 6.4 |
| $Y_2O_3$[b] | 0.3 | 0.3 | | 0.7 | 0.6 | 1.1 | 2.2 | 2.8 | 2.6 | 1.3 | 1.6 |
| CaO[d] | 0.2 | 0.2 | 0.3 | 0.20 | 0.30 | 0.20 | 0.15 | 0.2 | 0.2 | 0.3 | 0.9 |
| SrO[c,d] | 0.6 | 0.6 | n.d. | 0.10 | 0.2 | 0.1 | 0.05 | 0.2 | 0.1 | 0.1 | 0.2 |
| $H_2O$ (+ 100° C) | 1.2 | 1.1 | 0.05 | n.d. | 1.2 | 1.3 | n.d. | 0.9 | 0.9 | w.d. | n.d. |
| Insoluble | 1.0 | 1.0 | — | 3.0 | 2.4 | 2.9 | 2.1 | 1.0 | 2.0 | 0.2 | 9.1 |
| | 101.2 | 100.4 | 99.31 | 99.25 | 100.3 | 100.9 | 98.30 | 99.9 | 99.8 | 97.7 | 97.1 |
| S.G. | 4.42 | 4.41 | 4.46 | 4.42 | 4.50 | 4.43 | | | | | |

All analyses are on a moisture free basis. Ba was detected spectrographically in all samples in amounts less than 0.05 percent. No alkalies or MgO were detected.

[a] "Undetermined" was obtained by difference from the weight of components precipitated by ammonia after subtracting the weight of known components. The undetermined fraction is probably mainly $Al_2O_3$ but would also contain, $ZrO_2$, BeO, $Nb_2O_5$, $Ta_2O_5$ if present.

[b] Total $Ln_2O_3$ + $ThO_2$ + $Y_2O_3$ were determined chemically. $ThO_2$ was determined in davidite by Dr. K. Norrish, C.S.I.R.O. Division of Soils, Adelaide, using an X-ray fluorescence method. Individual lanthanons and yttria in oxides were determined spectrographically by A. B. Timms, South Australian Department of Mines, Research and Development Branch.

[c] X-ray fluorrescence analysis of davidite by K. Norrish.

[d] Spectrographic analysis of davidite by A. B. Timms.

*Description of Samples*

1. Tete, Mozambique. From one specimen weighing about 50 g. Lustre submetallic with extremely hackly fracture, very like chromite in appearance.
2. Same, from large representative sample all of which exhibited the typical high glassy lustre and conchoidal fracture of rare earth minerals.
3. Same, as recorded by Bannister & Horne (3) and included here for comparison. Also contained $ZrO_2$ 0.4, $Na_2O$ 0.15, $SiO_2$ 0.06%. MgO, $Nb_2O_5$ and $Ta_2O_5$ not found. Analysed by W. Ryan and P. J. Maple, Chemical Research Laboratory, Teddington, Middlesex, England.
4. Radium Hill (Olary) South Australia—From random samples of ore from old workings.
5. Same. From near surface, "David" lode. Also contained $Nb_2O_5$, less than 0.1 percent.
6. Same. From "Whip" lode, 100 foot level. Also contained $Nb_2O_5$, less than 0.1 percent.
7. Kalabity homestead, 30 miles NNW of Radium Hill. From a pegmatite outcrop.
8. Mount Pleasant, Hundred of Talunga, South Australia. From pegmatite. Also contained $Nb_2O_5$, 0.15 percent.
9. Same. Also contained $Nb_2O_5$, less than 0.1 percent.
10. Hundred of Jutland, South Australia. About three miles from Mt. Pleasant deposit. Pegmatite outcrop
11. Radium Hill. 700 foot level. This sample exhibited no signs of oxidation or weathering, hence it is more likely to represent davidite in its original form. The amounts of impurities were somewhat higher than usual and consisted mainly of rutile and quartz. Also contained $Ta_2O_5$, $Nb_2O_5$ less than 0.2 percent, $ZrO_2$ 0.3 percent.

TABLE 4

LANTHANONS AND YTTRIA IN DAVIDITE

| | 1 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|
| | Distribution, percent | | | | | | | | |
| $La_2O_3$ | 49 | 47 | 47 | 45 | 37 | 32 | 32 | 40 | 36 |
| $Ce_2O_3$ | 39 | 35 | 35 | 32 | 34 | 22 | 28 | 25 | 25 |
| $Pr_2O_3$ | 0.7 | 1.0 | 0.8 | 1.2 | 0.3 | 1.5 | 1.0 | 1.8 | 0.5 |
| $Nd_2O_3$ | 2.3 | 1.7 | 1.4 | 2.1 | 1.0 | 4.0 | 4.8 | 4.5 | 2.2 |
| $Sm_2O_3$ | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 | 0.5 | 0.2 | 0.5 |
| $Eu_2O_3$ | 0.03 | 0.03 | 0.03 | 0.03 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| $Gd_2O_3$ | 0.23 | 0.23 | 0.23 | 0.35 | 0.6 | 0.5 | 1.3 | 0.4 | 0.4 |
| $Tb_2O_3$ | 0.12 | 0.23 | 0.17 | 0.23 | 0.3 | 0.4 | 1.0 | 0.4 | 0.2 |
| $Dy_2O_3$ | 0.7 | 1.7 | 1.4 | 2.1 | 2.3 | 4.5 | 3.8 | 3.5 | 5.7 |
| $Ho_2O_3$ | 0.2 | 0.2 | 0.2 | 0.3 | 0.7 | 1.1 | 0.9 | 0.8 | 2.8 |
| $Er_2O_3$ | 0.6 | 1.7 | 2.3 | 2.3 | 2.3 | 5.3 | 3.3 | 2.3 | 3.0 |
| $Tm_2O_3$ | 0.1 | 0.2 | 0.3 | 0.2 | — | 0.5 | — | — | 0.2 |
| $Yb_2O_3$ | 1.2 | 1.7 | 2.2 | 2.2 | 2.7 | 6.0 | 4.8 | 5.7 | 2.3 |
| $Lu_2O_3$ | 0.3 | 0.3 | 0.3 | 0.5 | 0.5 | 0.8 | 0.5 | 0.6 | 1.4 |
| $Y_2O_3$ | 5.0 | 9.0 | 9.0 | 11.4 | 18.0 | 21.0 | 18.0 | 15.0 | 19.7 |
| Weighted Avg. mol. wt. $La_2O_3$ to $Lu_2O_3$ | 329 | 331 | 332 | 332 | 333 | 339 | 338 | 337 | 338 |

exhibited by the South Australian davidites. The analyses are in close agreement with that recorded by Bannister and Horne (analysis 3) except that chromium is higher and titanium lower.

*Distribution of Rare-earths.*—Table 4 shows the distribution of the individual lanthanons and yttria obtained by spectrographic analysis of the rare earth oxides separated from the davidite samples.

The distribution is similar to that suggested by Dixon and Wylie (4) in that there is an accumulation of lanthanons at each end of the series and lanthanum is in excess of cerium. The relative amounts of "light" and "heavy" lanthanons vary considerably and in general the amounts of yttria are closely related to the "heavy" group.

TABLE 5

RELATIVE PROPERTIES OF LIGHT AND HEAVY LANTHANONS AND YTTRIA

| | Mozambique | Radium Hill | | Mt. Pleasant | Kalabity H.S. |
|---|---|---|---|---|---|
| | | (a) | (b) | | |
| La-Tb | 92% | 82% | 65% | 66% | 73% |
| Dy-Lu | 3% | 8% | 15% | 15% | 9% |
| Y | 5% | 10% | 20% | 19% | 18% |

(a) Samples from 100 ft. level and above.
(b) Recent sample from 700 ft. level.

The relative proportions of the light and heavy lanthanons and yttria in davidite from four localities are shown in Table 5.

The distribution of the lanthanons in the davidite from the 700-foot level at Radium Hill is markedly different from that in the samples obtained from higher levels and the surface, and is very similar to that of the Mt. Pleasant davidite. It can be inferred from this that there is no definite lanthanon distribution peculiar to the davidite of any particular locality.

TABLE 6

RECALCULATED ANALYSIS FOR MT. PLEASANT DAVIDITE (NO. 8)

| | Percent | Mole wt. per unit cell | No. atoms | No. oxygens | Effective radius | |
|---|---|---|---|---|---|---|
| PbO | 0.3 | 15.97 | 0.072 | 0.072 | $Pb^{2+}$ | 1.21A |
| $UO_2$ | 1.5 | 79.84 | 0.296 | 0.592 | $U^{4+}$ | 0.97 |
| $Ln_2O_3$ | 9.6 | 511.01 | 3.014 | 4.521 | $Ln^{3+}$ | 1.0–1.18 |
| $V_2O_3$ | 2.8 | 149.04 | 1.318 | 1.977 | $V^{3+}$ | 0.93 |
| $ThO_2$ | 0.4 | 21.29 | 0.081 | 0.162 | $Th^{4+}$ | 1.02 |
| $Sc_2O_3$ | 0.1 | 5.32 | 0.078 | 0.117 | $Sc^{3+}$ | 0.81 |
| CaO | 0.2 | 10.64 | 0.190 | 0.190 | $Ca^{2+}$ | 0.99 |
| SrO | 0.2 | 10.64 | 0.102 | 0.102 | $Sr^{2+}$ | 1.13 |
| FeO | 26.0 | 1383.98 | 19.262 | 19.262 | $Fe^{2+}$ | 0.75 |
| MnO | 0.3 | 15.97 | 0.225 | 0.225 | $Mn^{2+}$ | 0.80 |
| $V_2O_3$ | 0.1 | 5.32 | 0.070 | 0.105 | $V^{3+}$ | 0.66 |
| $Cr_2O_3$ | 0.1 | 5.32 | 0.070 | 0.105 | $Cr^{3+}$ | 0.64 |
| $TiO_2$ | 53.1 | 2826.51 | 35.376 | 70.752 | $Ti^{4+}$ | 0.68 |
| $Al_2O_3$ | 2.8 | 149.04 | 2.924 | 4.386 | $Al^{3+}$ | 0.50 |
| | 97.5 | | | 102.46 | | |

$$\frac{5{,}190}{97.5} = 53.23.$$

*Constitution of Davidite.*—As a basis for calculating the contents of a unit cell of davidite, the data of Pabst and Thomssen (5) were used. According to these authors, davidite probably belongs to the space group R3 or $R\bar{3}$ with the following cell dimensions—

$$\text{(hexagonal)} - c_0 = 20.85\ \text{Å}, \quad a_0 = 10.36\ \text{Å}.$$

The molecular contents of the unit cell were calculated from the formula given by Clark and Duane (6).

$$\rho = \frac{n\,(M \times 1.649 \times 10^{-24})}{\frac{1}{2}\sqrt{3}\,C \times a_0^3}$$

where $\rho$ = specific gravity of davidite; $n$ = number of molecular units per unit cell, for $R\bar{3}$, $n = 3$; $M$ = molecular weight per unit; $C = \frac{c_0}{a_0}$.

The calculated cell content n M, using a value of 4.42 for the S.G. of davidite, was 5,190 and all the analyses were recalculated on this basis.

The recalculated analysis for number 8 is shown in Table 6, all others being treated in a similar manner.

The components were expressed in their usual lower oxidation states, water and "insoluble" being excluded. The calculation of iron as FeO is considered to be justified by the high value for sample number 11, which was obtained from a relatively unweathered zone of the Radium Hill ore body.

TABLE 7

ARRANGEMENT OF ATOMS IN GROUPS

Case 1 A = Pb, U, Ln, Y, Th, Sc, Ca, Sr, Fe, Mn.
B = Ti, Cr, V, Al.
O = oxygen.

| Group | No. 1 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | Arith. mean | Std dev. | Coeff. of variation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 22.39 | 23.11 | 25.80 | 26.27 | 24.78 | 24.67 | 24.64 | 24.80 | 25.14 | 23.51 | 24.51 | 1.19 | 4.9 |
| B | 38.46 | 37.13 | 35.38 | 34.14 | 36.43 | 37.92 | 38.44 | 37.57 | 35.70 | 39.10 | 37.03 | 1.60 | 4.3 |
| O | 99.04 | 99.67 | 97.52 | 96.59 | 98.94 | 101.44 | 102.46 | 101.61 | 98.46 | 100.79 | 99.65 | 1.90 | 1.90 |

Case 2 A = Pb, U, Ln, Y, Th, Sc, Ca, Sr.
B = Fe, Mn, Ti, Cr, V, Al.
O = Oxygen.

| Group | No. 1 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | Arith. mean | Std dev. | Coeff. of variation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 4.78 | 4.22 | 4.77 | 4.94 | 5.47 | 5.24 | 5.15 | 5.27 | 5.01 | 5.76 | 5.06 | 0.42 | 8.3 |
| B | 56.07 | 56.02 | 56.41 | 55.47 | 55.74 | 57.35 | 57.93 | 57.10 | 55.83 | 56.85 | 56.47 | 0.80 | 1.4 |
| O | 99.04 | 99.67 | 97.52 | 96.59 | 98.94 | 101.44 | 102.46 | 101.61 | 98.46 | 100.79 | 99.65 | 1.90 | 1.90 |

Case 3 A = Pb, U, Ln, Y, Th, Sc, Ca, Sr.
B = Fe, Mn.
C = Ti, V, Cr, Al.
O = Oxygen.

| Group | No. 1 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | Arith. mean | Std dev. | Coeff. of variation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 4.78 | 4.22 | 4.77 | 4.94 | 5.47 | 5.24 | 5.15 | 5.27 | 5.01 | 5.76 | 5.06 | 0.42 | 8.3 |
| B | 17.61 | 18.89 | 21.03 | 21.33 | 19.31 | 19.43 | 19.49 | 19.53 | 20.13 | 17.75 | 19.45 | 0.95 | 4.9 |
| C | 38.46 | 37.13 | 35.38 | 34.14 | 36.43 | 37.92 | 38.44 | 37.57 | 35.70 | 39.10 | 37.03 | 1.60 | 4.3 |
| O | 99.04 | 99.67 | 97.52 | 96.59 | 98.94 | 101.44 | 102.46 | 101.61 | 98.46 | 100.79 | 99.65 | 1.90 | 1.90 |

For space group R3 the number of atoms per unit cell should be divisible by 3, the indicated compositions for the possible combinations thus being: Case 1—$A_6$, $B_{12}$, $O_{22}$. Case 2—$A_2$, $B_{19}$, $O_{32}$. Case 3—$A_2$, $B_6$, $C_{13}$, $O_{22}$.

The suggestion of Bannister and Horne (3) that iron should be allocated according to its oxidation states is not supported by variations shown in the probable values for ferrous iron in davidites of otherwise similar composition. This is shown by numbers 1 and 2 and 8 and 9 respectively in Table 2. The ferrous iron figures differ considerably in each pair although the analyses are otherwise almost identical. The lanthanons were regarded as all trivalent and in calculating molecular and ionic ratios the average molecular weights shown in Table 4 were used. Strontium was present in all samples and was

included in the same group as calcium. The lead was assumed to be radiogenic and was included with uranium. Scandium was also included with the lanthanons and uranium while "undetermined" was regarded as $Al_2O_3$ and included with Ti, V and Cr.

In determining the probable distribution of the components within the unit cell, use was made of ionic radii and known affiliations. Thus, Pb, U, Ln, Y, Th, Sc, Ca and Sr, are usually grouped together as are Ti, Cr, V and Al. The position occupied by Fe and Mn is doubtful since they could enter into either position on the basis of atomic radii.

Three cases can therefore be considered for the distribution of the atoms depending on the position allotted to Fe, Mn.

In addition to occupying positions in either of the groups containing the other elements it is possible that they may occupy a special position of their own, thus forming a third group. The possible arrangements are shown in Table 7.

If davidite has the composition indicated in case 1, then it probably belongs to the system of multiple oxides classified by Palache et al (7) as:

$$Am\ Bn\ Xp$$

where $m:n$ is from 2:3 to 3:5.

This group includes arizonite ($Fe_2Ti_3O_9$) and brannerite, the latter commonly being found in close association with davidite in South Australia. It is interesting also that if the formula for arizonite is written with all the iron in the ferrous state, it then becomes:

$$Fe_2Ti_3O_8 \quad \text{or} \quad Fe_8Ti_{12}O_{32}$$

which closely resembles that proposed in case 1 for davidite.

In the absence of quantitative data relating to the composition of the unit cell, it is not possible to decide on any particular arrangement and either of the other two proposed formulae may be correct.

The comparatively low mean value for group A in cases 2 and 3 could be due to several factors. The impurities in the davidite samples generally consist of iron- and titanium-bearing minerals and this would result in a relative increase in the atomic totals for the other groups. On the other hand group A may exhibit "defect" structure due to replacement of two atoms of trivalent lanthanons by one of quadrivalent uranium.

## CONCLUSION

Results of numerous analyses indicate that davidite is a homogeneous mineral in which uranium and the lanthanons are isomorphously replaceable as are probably titanium, vanadium, chromium and aluminium. No definite composition can be proved owing to uncertainty of the position occupied by iron but davidite could be related to arizonite and brannerite.

The results do not support the theory advanced by Whittle that davidite is a heterogeneous mixture of rutile with one or more radioactive constituents.

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RESEARCH AND DEVELOPMENT BRANCH,
S. AUSTRALIAN DEPT. OF MINES,
ADELAIDE, S. AUSTRALIA,
*Oct. 28, 1959*

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# EXTRACTABILITY OF HUMIC ACID FROM COALIFIED LOGS AS A GUIDE TO TEMPERATURES IN COLORADO PLATEAU SEDIMENTS[1]

IRVING A. BREGER AND JOHN C. CHANDLER

ABSTRACT

Coalified logs in Triassic and Jurassic sediments of the Colorado Plateau have been exposed to alkaline ground water. Extraction of humic acids under such conditions is temperature dependent. Study of residual humic acids in a suite of coalified logs has indicated that temperatures up to but not over 120° C prevailed in the sediments. This maximum temperature corresponds with that to be expected from geothermal gradient and estimated from mineralogic evidence.

## INTRODUCTION

MANY of the exploitable uranium deposits of the United States occur in Triassic and Jurassic sediments of the Colorado Plateau. Tree trunks, branches, and woody fragments, all of which have been assigned to the genus *Araucarioxylon* (6), were buried in these sediments and subsequently converted into lignite, subbituminous, or high-volatile bituminous A coal. It is reasonable to assume that coalification was essentially complete for Triassic wood during Triassic time, and for Jurassic logs during Jurassic time. Although there are differences of opinion, a considerable body of geological and geochemical evidence indicates that uranium was introduced into the sediments not earlier than during Late Cretaceous time (7, 9). A preliminary study of this coalified wood and its relation to uranium has already been completed (1).

There is abundant evidence that uranium was introduced into many parts of the Colorado Plateau in alkaline solution. Observation of re-entrants and of secondary growth on quartz grains points to solution and redeposition of silica. Strong evidence for alkalinity is derived from uranium-bearing impregnated sandstones, commonly called "uraniferous asphaltites," where solution of silica and deposition or precipitation of organic matter seemingly occurred simultaneously to give an impression of quartz replaced by organic matter. In all probability the uranium was carried in the form of a uranyl carbonate complex, an example of which is $Na_4[UO_2(CO_3)_3]$ (3).

As has previously been noted, contact of a solution carrying a complex uranyl carbonate ion with a coaly environment where the pH is between 2.2 and 4.5 will result in decomposition of the complex and absorption of the uranyl ion (2, 3). If the uranium-bearing solution or a nonuraniferous alkaline ground water were to contact the coalified wood at elevated tempera-

[1] Publication authorized by the Director, U. S. Geological Survey.

tures, the heated alkaline solution would undoubtedly dissolve and remove from the coal any available humic acid. With this in mind, studies have been conducted to determine the quantity of humic acid still present in coalified logs containing various percentages of uranium in an attempt to establish the maximum temperatures to which these logs and the enclosing sediments were subjected. Obviously, any conclusions from this work would be based on an implied contact of alkaline solution with the coal. Broad initial occurrence of calcite in the sediments and evidence for its subsequent redistribution, however, provide ample additional evidence for long-term alkaline conditions.

## SAMPLES

A number of restrictions were placed on samples to be used for this study. As noted below, the 30-gram requirement immediately limited the specimens to those for which sufficient material was available. Moreover, only those samples with rank equivalent to high-volatile A bituminous were chosen in order to eliminate variabilities in results caused by variation in rank. One exception to this restriction is to be found in sample H, the equivalent rank of which is high-volatile B bituminous. The slight difference in rank between this sample and the others was disregarded inasmuch as this represented one of the two samples with high uranium content available in sufficient quantity.

As shown in Table 1, uranium contents for the first seven samples ranged from 0.0005 to 7.54 percent. Samples G and H, which had the highest percentages of uranium, also had extremely high percentages of organic sulfur (6.51 and 9.92%, respectively). Sample J (Table 1) is a high-volatile A bituminous coal from Kentucky carried through the experimental procedure for comparison.

Four of the samples (A, B, C, and H) were from the Moss Back member of the Chinle formation (Triassic) and were collected in uranium mines of the Temple Mountain area, San Rafael Swell, Emery County, Utah. Sample G was taken from the Lucky Strike No. 2 mine, on the west side of the San Rafael Swell, and is closely related to the above four samples.

Samples D, E, and F were collected in uranium mines in the Salt Wash sandstone member of the Morrison formation (Jurassic).

All samples used were of unoxidized coalified wood.

Each specimen was handpicked, where necessary, to remove extraneous mineral matter and then crushed to fragments smaller than 1 inch. These pieces were carefully examined for adhering mineral matter, mostly quartz, pyrite, and some calcite, which was removed using a small grinding tool equipped with a thin abrasive wheel. Care was taken to prevent rapid grinding and excessive heating of the coal. After cleaning, the coal was crushed to pass a 50-mesh screen and quartered. One split of each sample was submitted to the U. S. Bureau of Mines for standard coal analysis, and the remainder was used for uranium analysis and for the experimental work described below.

Each sample was refluxed with 2 *N* hydrochloric acid for six hours, filtered on a Büchner funnel, and washed until the effluent reached pH 6. This

TABLE 1

CHEMICAL ANALYSES OF COALS

| Sample[4] | Total S, %[1] | Organic S, %[1] | BTU[1] | Volatile matter, %[1] | Carbon, %[1] | Hydrogen, %[1] | Oxygen, %[1] | Nitrogen, %[1] | Ash, %[2] | Uranium, %[3] |
|---|---|---|---|---|---|---|---|---|---|---|
| A | 4.5 | 1.31 | 14,990 | 70.4 | 78.5 | 6.8 | 9.8 | 0.4 | 5.2 | 0.0005 |
| B | 2.4 | 1.33 | 15,340 | 72.5 | 81.2 | 7.1 | 8.9 | 0.4 | 3.1 | 0.015 |
| C | 3.9 | 2.12 | 15,380 | 70.5 | 79.5 | 7.1 | 8.9 | 0.6 | 6.8 | 0.015 |
| D | 1.0 | 0.50 | 14,260 | 39.9 | 79.7 | 5.0 | 14.0 | 0.3 | 3.8 | 0.080 |
| E | 1.5 | 0.56 | 14,700 | 49.5 | 80.2 | 5.6 | 12.5 | 0.2 | 6.3 | 0.14 |
| F | 2.0 | 0.53 | 15,060 | 48.4 | 82.2 | 5.8 | 9.7 | 0.3 | 5.1 | 0.38 |
| G | 7.8 | 6.51 | 14,420 | 37.9 | 78.6 | 5.1 | 8.1 | 0.4 | 8.5 | 1.15 |
| H | 11.4 | 9.92 | 13,600 | 32.2 | 75.6 | 4.0 | 8.8 | 0.2 | 22.9 | 7.54 |
| J | 0.7 | — | 14,790 | 39.8 | 82.4 | 5.6 | 9.6 | 1.7 | 1.7 | — |

[1] Analyses by U. S. Bureau of Mines, Pittsburgh, Pennsylvania, on a moisture- and ash-free basis.

[2] Analyses by U. S. Bureau of Mines, Pittsburgh, Pennsylvania, on a moisture-free basis.

[3] Moisture-free basis; analyses by staff of U. S. Geological Survey.

[4] A. Collection No. SSB-2-56. Sample from North Mesa No. 2 mine, Temple Mountain area, Emery County, Utah.

B. Collection No. SSB-8-56. Sample from North Mesa No. 9 mine, Temple Mountain area, Emery County, Utah. Log collected in Moss Back member of Chinle formation (Triassic).

C. Collection No. SSB-3-56. Same source as sample A.

D. Collection No. SSB-29-56. Sample from Peanut mine, T. 30 N., R. 17 W., Montrose County, Colorado. Log from Salt Wash sandstone member of Morrison formation (Jurassic).

E. Collection No. SSB-33-56. Sample from Virgin No. 3 mine, sec. 21, T. 29 S., R. 101 W., Montrose County, Colorado. Log from Salt Wash sandstone member of Morrison formation (Jurassic).

F. Collection No. SSB-31-56. Same source as sample D.

G. Collection No. SSB-26-56. Sample from Lucky Strike No. 2 mine, west side of San Rafael Swell, Emery County, Utah. Coalified plant stems from Moss Back member of Chinle formation (Triassic).

H. Collection No. IAB-36B-1B. Sample from Rex No. 1 mine, Temple Mountain area, Emery County, Utah. Log from the Moss Back member of the Chinle formation (Triassic).

J. High-volatile A bituminous coal from Elkhorn No. 3 mine, Breathitt County, Kentucky. Sample made available by Mr. Guy E. Hoover, Chesapeake and Ohio Railway Company.

procedure was used to strip any ion-exchanged elements from the coal and to make the humic constituents available for extraction. The air-dried (60°-70° C) coal was then treated with benzene in a Soxhlet extractor until the extract was colorless indicating that the removal of waxes and resins was complete. The final product was dried under vacuum at about 95° C to remove any residual benzene and water.

To each coal (approximately 30 g) was added 200 ml of 0.1 *N* sodium hydroxide and the mixture, in a 500-ml Florence flask, was placed in a large electrically-controlled autoclave. The temperature was adjusted to 100° C, and the autoclave and contents were agitated four hours to assure maximum contact between the coal and alkali. At the end of this period the cooled samples were filtered on a glass fiber filter pad and the residual coal was washed with fresh 0.1 *N* sodium hydroxide. The filtrate was adjusted to 500 or 1,000 ml in a volumetric flask and stored under nitrogen.

The wet filtered coal, including the glass fiber filter pad, was returned to the flask, additional 0.1 *N* sodium hydroxide was added, and a second extraction was made at 110° C. The identical procedure was carried through at 120°, 130°, and 140° C, the maximum operating limit of the autoclave. Runs at 150° C were carried out using stainless steel pressure bombs wrapped in heating tapes and placed on an oscillating table to assure complete contact between the coal and alkali. The temperature of the contents in each bomb was measured by a thermocouple inserted in a well in the bomb wall. The limited capacity of the high pressure vessels made it desirable to divide each sample into two equivalent portions, each of which was placed in a separate bomb.

TABLE 2

MILLIGRAMS OF HUMIC ACID EXTRACTED PER GRAM OF ORIGINAL COAL AT VARIOUS TEMPERATURES

| Sample | Extraction temperature | | | | | |
|---|---|---|---|---|---|---|
| | 100° C | 110° C | 120° C | 130° C | 140° C | 150° C |
| A | 2.06 | 4.14 | 2.16 | 1.24 | 4.28 | 3.38 |
| B | 0.51 | 1.09 | 0.21 | 0.50 | 0.61 | 0.80 |
| C | 1.64 | 1.78 | 1.18 | 0.72 | 2.28 | 2.94 |
| D | 7.13 | 2.40 | 1.36 | 2.36 | 2.82 | 1.92 |
| E | 2.09 | 2.61 | 0.76 | 1.99 | 2.89 | 5.44 |
| F | 1.09 | 0.00 | 0.35 | 0.00 | 3.18 | 0.86 |
| G | 1.83 | 1.26 | 0.88 | 1.36 | 2.30 | 3.33 |
| H | 2.24 | 0.50 | 0.46 | 0.89 | 1.71 | 3.02 |
| J | 6.42 | 0.57 | 0.60 | 0.00 | 0.00 | 1.78 |

The strength of the alkaline solution used for extraction in the laboratory is undoubtedly much greater than that which prevailed under geologic conditions. The purpose of this study, however, was to extract residual humic acid from the coal samples, and for this reason it was desirable to use a minimum volume of solution that would effect maximum solubility of the humic substances.

Aliquots of each extract (100°, 110°, 120°, 130°, 140°, and 150° C) were analyzed for organic carbon by the permanganate oxidation technique developed by Kreulen (5), and following his procedure and conversion curve, the number of milligrams of humic acid extracted per gram of original coal was calculated. Each analysis was carried out at least in duplicate. Data are shown in Table 2.

To verify the factor recommended by Kreulen for conversion of organic carbon to humic acid, an analysis was conducted on a sample of humic acid isolated from peat from the Cedar Creek Bog, Anoka and Isanti Counties, Minnesota.[2] This humic acid contained 57.17 percent carbon and 4.43 percent hydrogen on a moisture- and ash-free basis. A sample of the material containing 6.5 percent moisture and 5.7 percent ash on a moist basis was dis-

[2] The peat was kindly made available by Professor F. Swain, University of Minnesota.

solved in alkali to prepare a solution containing 1.0 g of as-is humic acid per liter. Corrected for moisture and ash, this solution actually contained 0.88 g of humic acid per liter. Aliquots of the solution were analyzed by Kreulen's technique to yield values of 0.90, 0.91, 0.90, and 0.88 grams of humic acid per liter, giving an average value of 0.90 and an absolute accuracy of 2.3 percent. The analytical method was, therefore, considered adequate for these studies.

## DISCUSSION AND SUMMARY

Because low rank coal contains acidic constituents, treatment with alkali at any temperature should result in the extraction of some part of the coal substance. Extraction at 100° C should, therefore, remove all humic con-

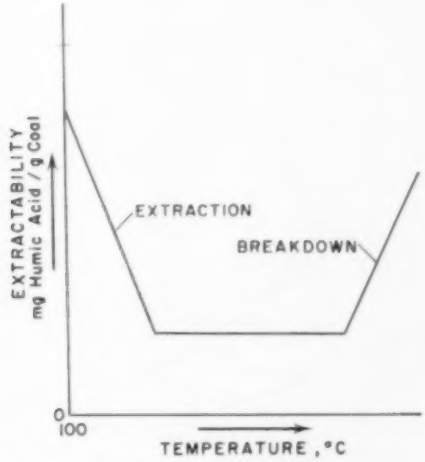


FIG. 1. A theoretical curve for extraction of coal.

stituents soluble up to that temperature. Continued extraction at 110° C will then dissolve those coal constituents soluble at 110° C but not soluble at 100° C, a relatively smaller quantity. At some higher temperature, the alkali might be expected to effect chemical changes in the coal structure leading to molecular breakdown and increased extractability. The features of a theoretical extraction curve are illustrated in Figure 1. As shown in Figure 2, the extraction curve for sample J, a high-volatile A bituminous coal used as a standard, follows this pattern very closely. Were this coal pre-extracted *in situ* by an alkaline solution under natural conditions, then the large amount of extractable humic matter normally present would have been removed and the curve would have been expected to take on the shape shown for sample A in Figure 2.

It is apparent that sample A has been pre-extracted under natural con-

ditions at 100° C with removal of most of the coal substance normally soluble at that temperature leaving only 2.06 mg/g (0.206 percent) available for extraction under the experimental conditions used. Although the shape of the curve makes it seem unlikely that any appreciable extraction had occurred at 110° C, it is not possible to determine from the position of the point along the ordinate at 110° C for sample A if this sample had been extracted at that

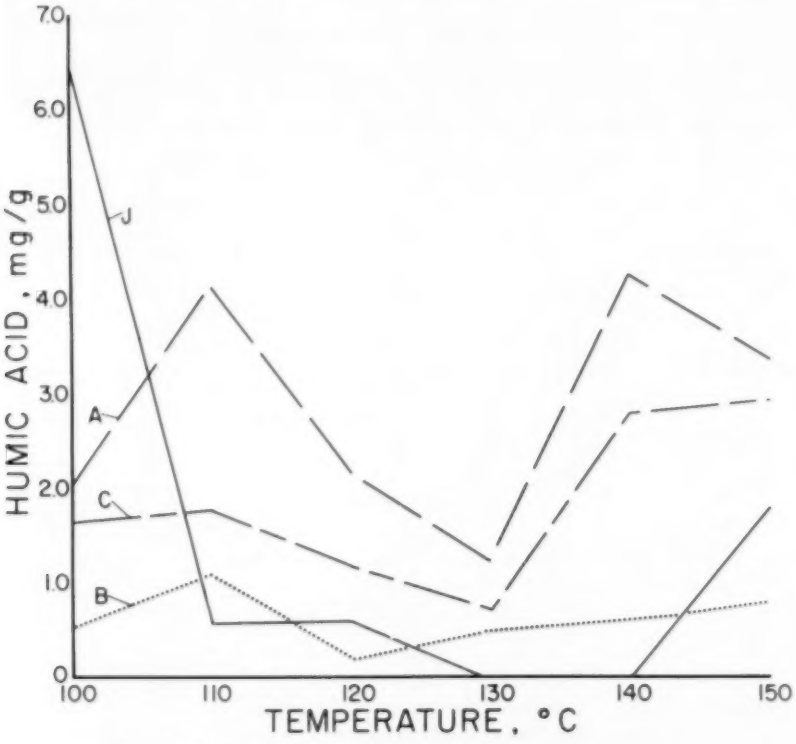


FIG. 2. Extractability of samples A, B, C, and J by alkali.

temperature. For this reason, it cannot be stated with assurance that sample A had not been affected by alkaline solutions at 110° C, and can only be concluded that the temperature to which the coalified log had been subjected in the presence of an alkaline solution was above 100° C, but probably lower than 110° C.

The same considerations hold in analysis of the curves for samples B and C (Fig. 2). In both cases, the decrease in material extractable at 100° and 110° C can be interpreted to show that these samples were pre-extracted under natural conditions above 110° C but probably lower than 120° C.

Extraction patterns for samples D and F are shown in Figure 3. The extractability of sample D is nearly identical to that of the standard coal (sample J) and indicates that this coal (D) was probably not extracted at all. Sample F appears to have been extracted to some extent at 100° C or below, but certainly not over that temperature. These two samples are from the same mine and the data with regard to temperature correlate particularly well.

Sample E, from the Virgin No. 3 mine, appears to have been strongly extracted *in situ* at 100° C, and may have been extracted at 110° C. Indications are that coals G and H may have been pre-extracted at temperatures up to but not over 100° C.

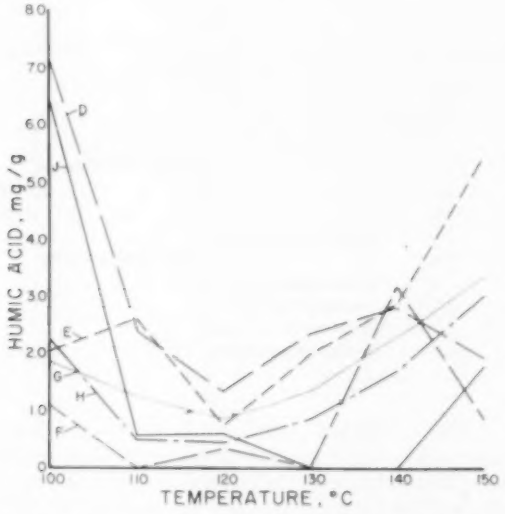


FIG. 3. Extractability of samples D, E, F, G, H, and J.

Conclusions regarding the temperatures at which the coal samples appear to have been extracted by alkaline solutions under geological conditions are summarized in Table 3. Perhaps because of the limitation in the number of samples available for this work, it is not possible to recognize any clear relation between temperature and uranium content. It is interesting, however, that those samples with highest uranium contents have the lowest indicated temperatures. It is possible that radiation from the uranium and its daughter products may have led to the formation of sufficient coal fragments of low molecular weight to result in misinterpretation of the curves for samples G and H. On the other hand, there is nothing about these curves to indicate that the coals were ever exposed to temperatures above 120° C. Also, it must again be noted that samples G and H have unusually high organic sulfur contents (6.51 and 9.92 percent, respectively) which may and probably do

lead to incompletely understood changes in coal structure. These changes may well alter the extractability characteristics of the humic acid.

Weeks and Garrels (8) have pointed out that the Jurassic and Triassic sediments of the Colorado Plateau were buried under about 5,000 and 10,000 feet of sediment, respectively, by the end of the Cretaceous. If a surface temperature of 20° C and a geothermal gradient of 1° C per 100 feet is assumed, temperatures in the sediments would be expected to approximate 120° C. The temperatures indicated in Table 3 all lie below 120° C in keeping with the calculated temperature. Coleman (4), moreover, concluded from mineralogic evidence that temperatures lower than 140° C prevailed in the sediments.

TABLE 3

SUMMARY OF TEMPERATURES OF SEDIMENTS AS INDICATED BY EXTRACTABILITY STUDIES

| Sample | Age | Urnaium, percent | Under 100° C | 100°–110° C | 110°–120° C |
|---|---|---|---|---|---|
| A | Triassic | 0.0005 | | ——— | |
| B | Triassic | 0.009 | | | ——— |
| C | Triassic | 0.015 | | | ——— |
| D | Jurassic | 0.080 | ——— | | |
| E | Jurassic | 0.14 | | ——— | |
| F | Jurassic | 0.38 | ——— | | |
| G | Triassic | 1.15 | ——— | | |
| H | Triassic | 7.54 | ——— | | |
| J | Pennsylvanian | — | ——— | | |

The limited number of coal samples available for the current study precludes any generalization regarding temperatures and uranium mineralization. If uranium is disregarded, however, it can be stated that the coalified wood samples studied have not been extracted *in situ* by alkaline solutions at temperatures above 120° C. Study of the coalified wood has resulted, therefore, in the establishment of a maximum temperature, by a completely new technique, that corresponds extremely well to that calculated from considerations of geothermal gradient and mineralogic evidence.

This work is part of a program conducted by the U. S. Geological Survey on behalf of the Division of Research, U. S. Atomic Energy Commission.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.,
*August 24, 1959*

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# CURRICULAR AND PROFESSIONAL ASPECTS OF GEOLOGICAL ENGINEERING[1]

J. M. NEILSON, A. K. SNELGROVE, AND J. R. VAN PELT

ABSTRACT

The Geological Engineering curriculum, recognized for over thirty years by the Engineers' Council for Professional Development, is still suspect in some quarters because of its relative emphasis on basic rather than engineering sciences.

An interdepartmental committee of broad scope at Michigan Tech has spent a year on a critical study of the make-up of the curriculum in question with a view to putting it on a firmer basis within the engineering profession as well as within the geological fraternity. This article endeavors to define adequately the scope and function of the Geological Engineer. To improve the integration of engineering and geology and to establish the validity of this discipline, a quantitative portrayal is advanced of the impingement of each on the other.

## INTRODUCTION

THIS paper is the outgrowth of studies recently undertaken at the Michigan College of Mining and Technology in an effort to find solutions to certain problems facing Geological Engineering. These problems are compounded from several circumstances: (1) the reservation formerly expressed by the Engineers' Council for Professional Development[2] regarding its acceptance of Geological Engineering as a bona fide branch of engineering, (2) the misunderstanding sometimes observed within the geological and the mining engineering professions of the relationship between Geology and Geological Engineering, and (3) the lack of an adequate definition of Geological Engineering.

An interdepartmental Committee on the Engineering Content of Geology and Geological Engineering was established at Michigan Tech in October 1957 to investigate these problems and to recommend possible solutions. The Committee is composed of representatives of Michigan Tech's Departments of Geology and Geological Engineering, Mining Engineering, Civil Engineering, Physics, and Engineering Mechanics. Frank Kerekes, Dean of the Faculty, and M. E. Volin, Director of the College's Institute of Mineral Research, contributed to the Committee's discussions from time to time.

The paper may be regarded as an interim report of the Committee. It is the writers' hope that the statements contained in it may serve to clarify the purpose and function of Geological Engineering as well as to provide a basis for future discussions.

[1] Presented at AIME Annual Meeting, New York, February 1958; up-dated and revised to December 1958.

[2] This refers to the designation of "cognate" or "fringe" curricula proposed in a resolution by the Education Committee of ECPD in 1954(1). The designation was later withdrawn.

## GENERAL CONSIDERATIONS

The current status of Geological Engineering has become a matter of concern to AIME's Council of Education and its Geological Engineering Education Committee, to college and university administration and teaching divisions, and to many individuals in the geological profession. It is not too much to say that certain disquieting developments have brought about a state of apprehension in several quarters. Many of Geological Engineering's difficulties seem to stem from uncertainty as to its scope and the failure of its practitioners to define its function.

Several persons influential in ECPD have either voiced or implied their doubts as to the validity of Geological Engineering as a branch of the professional field of engineering. The stated primary objective of ECPD is to enhance the status of the engineering profession by various methods of improving the selection, guidance, training, and recognition of the members of the profession. Accreditation of engineering curricula is an important means of carrying out this objective and, to date, nineteen Geological Engineering curricula have been accredited. Future accreditation procedures may eliminate Geological Engineering from the recognized fields of engineering unless those who practice it take effective steps to justify its retention. The doubts about Geological Engineering typically are based, not on any question as to quality of instruction, but on the feeling by some that the curricula do not contain a sufficient engineering emphasis and sequence.

In this connection, the ASEE Committee on Evaluation of Engineering Education proposed, in its final report (3), the quantitative structure of curricular content as related to the objectives of engineering education. In harmony with these proposals, ECPD adopted its "Additional Criteria," which in their revised form (2) constitute a useful guide both to curricular content and to the sequential relationship of the various parts of the curriculum.

Fortunately, the Additional Criteria contain ample flexibility to accommodate all true engineering curricula irrespective of fields of specialization. It is to be hoped that accrediting committees give full heed to this flexibility when judging the time devoted to engineering sciences and engineering analysis, design, and systems. The Geological Engineering curriculum may well substitute subjects more directly related to its area of professional interest while still maintaining the essential characteristics of all engineering programs, and specifically the ability to design. This aspect of the Geological Engineering curriculum will be discussed later.

A major factor contributing to the lack of appreciation by members of the engineering profession of the training and functions of the Geological Engineer is our failure to provide an adequate explanation of our specialized endeavor. We—as Geological Engineers—must assume responsibility for this omission and we must establish the place that the Geological Engineer occupies in the engineering scheme of things.

## THE SCOPE OF GEOLOGICAL ENGINEERING

It has been said (4) that more confusion and misunderstanding concerning the relationship between Geology and Geological Engineering exist within the geological profession than outside it. The truth of this statement became apparent during the first few meetings of the Michigan Tech Committee when several of our non-geological colleagues were more willing to concede an engineering counterpart to geological science than were some of those more directly associated with geology.

Actually, the distinction between Geology as a science and Geological Engineering as an engineering discipline has long been recognized in the separate curricula in these fields as found in many institutions of higher education.

Some of the confusion within the geological profession may stem from the "pure" geologist's aloofness to the pragmatic approach of engineering analysis. Certainly the specialist in paleontology or theoretical mineralogy has little contact with engineering although engineering principles occasionally may be introduced even in these branches (cf. "Experiments on Relative Streamlining of Coiled Cephalopod Shells") (5).

Our interdepartmental Committee agreed that certain aspects of mineral industries development and civil engineering construction require specialized applications of geology for their successful execution. It is our thesis that these specialized geologic applications necessitate, or at least provide a proper place for, an engineering base as well as a scientific one.

One of the chief functions of the Geological Engineer in the mineral industries field is to design and execute comprehensive programs of exploration for mineral deposits. In many cases his responsibilities may continue beyond the several phases of exploration to participation in development and production planning. Advances in field applications of geophysics, geochemistry, and photogeology together with new methods of mineral extraction and ore beneficiation require men trained in the application and interpretation of these various methods and techniques. This training must go beyond the scope of the science or liberal arts geology curriculum and it should include specialized training in engineering disciplines. In this connection, the engineering aspects of mineral exploration have been reviewed at some length by Forrester (6).

Similarly, the engineering geology branch of Geological Engineering must be based upon a sound knowledge of geological science and a broad understanding of the engineering properties of geologic materials of all kinds. This specialized knowledge is applied to the siting, planning, and design of engineering works and to the selection and behavior of natural materials in all manner of civil engineering activities.

Specialized applications of geological science and engineering may be envisaged in several other areas such as geohydrology and military engineering but these are mainly offshoots from the larger fields of mineral resources development and civil engineering construction.

DEFINITION OF GEOLOGICAL ENGINEERING

It is clear that Geological Engineering involves more than application of geologic principles to the solution of engineering problems and, conversely, the application of engineering principles to the solution of geologic problems; it should also comprise an integration of the two applications.

With this purpose in mind, our Michigan Tech Committee proposes the following definition of Geological Engineering:

*"Geological Engineering is that profession in which a knowledge of geological sciences and engineering fundamentals gained by study, practice, and experience is applied to the exploration, development, and utilization of mineral resources, and to the location and construction of engineering projects for the benefit of mankind."*

Geological Engineering deals primarily with natural forces and materials and it involves evaluation and correlation of all pertinent data concerning them; it also involves synthesis of this information for design purposes. All of this is implied in the foregoing definition.

Geological Engineering, as the definition suggests, operates in:

a. Mineral exploration, development, and production; regardless of whether the product be metallic, nonmetallic, or fluid.
b. The construction industry, where it is concerned with the selection and behavior of rocks, unconsolidated sediments, and soils in projects involving surface and subsurface excavations, foundations, slope stability, erosion control, drainage, irrigation, groundwater, highway subgrades, and many others.
c. Other related fields.

Our definition is patterned after ECPD's definition of Engineering (*7*), and carries it specifically to Geological Engineering as a profession by delimiting the field of specialization.

At about the same time that the Michigan Tech Committee was formulating the foregoing definition, a special committee on Geological Engineering Education of the Council of Education, AIME, was also engaged in defining the field.[3]

The AIME committee submitted the following draft to the Council of Education, and the draft is awaiting action at the next meeting of the Council.

*Geological Engineering consists of the joint application of engineering and geological principles to the problems of analysis and design in those engineering activities directly related to the earth, its materials, structures, and forces.*

*1. As a branch of engineering, geological engineering:*
   *a. Deals with the materials and forces of nature for the benefit of man.*
   *b. Is built not only on the basic and engineering sciences common to all engineering branches but also on other sciences appropriate to its special field.*

[3] The AIME committee consisted of H. G. Botset, University of Pittsburgh, Chairman; S. A. Lynch, Texas A. & M.; J. R. Van Pelt, Michigan Tech; and E. H. Wisser, University of California.

*c. Involves the elements of analysis and design, which includes such activities as designing methods and procedures to be used in exploration for and development and production of economic deposits. This concerns the individual items or components and the larger units or systems involved.*

*2. Geological engineering operates in:*

*a. The mining and petroleum industries, where it is concerned with exploration, development, and research.*

*b. The construction industry, where it is concerned with bed rock, unconsolidated sediments, in transport as well as deposited, and soils.*

*c. Hydrology, where it is concerned with ground water, surface water, erosion, sediment transportation and deposition.*

The points of agreement between the two definitions are important:

1. They both imply an integration of geological sciences and engineering fundamentals, not merely their co-existence in a curriculum.
2. They both state that geological engineering is applied in two fields: mineral industries and civil engineering structures.

The most obvious point of difference is the separate consideration of "hydrology" (very broadly defined) in the AIME definition. In the Michigan Tech definition, this field is implicitly included in civil engineering works.

Another difference is that the AIME definition specifically covers application to "problems of analysis and design," while the Michigan Tech definition only implies such application.

## NOMENCLATURE

It may be appropriate at this point to distinguish between Geological Engineering and engineering geology. The similarity in nomenclature has led to much confusion both within and without the geological profession. Geological Engineering refers to a type of professional training which embraces both the earth sciences and the engineering sciences, and it is applied in both the mineral industry and the construction industry. The term "engineering geology" should be limited to the specialized application of geology in the civil engineering field and its related branches. It may be mentioned that The Geological Society of America has an active Division on Engineering Geology. The division's Teaching Aids Committee (of which the senior author is a member) defined the area of specialization in its 1957 report (8). The reader is referred to this source for further clarification.

There is also some confusion regarding nomenclature in the mineral industries area of Geological Engineering. "Applied geology," "mining geology," "petroleum geology," and "mineral exploration" have been variously applied to this area of geologic specialization, but these terms also have been used synonymously with Geological Engineering. It would seem preferable to use the term "mining geology" for geologic applications in the mining industry. This terminology is well established (6) although the meaning has not always been in the same sense. "Mining geology" also has the advantage of providing a definitive contrast to "engineering geology."

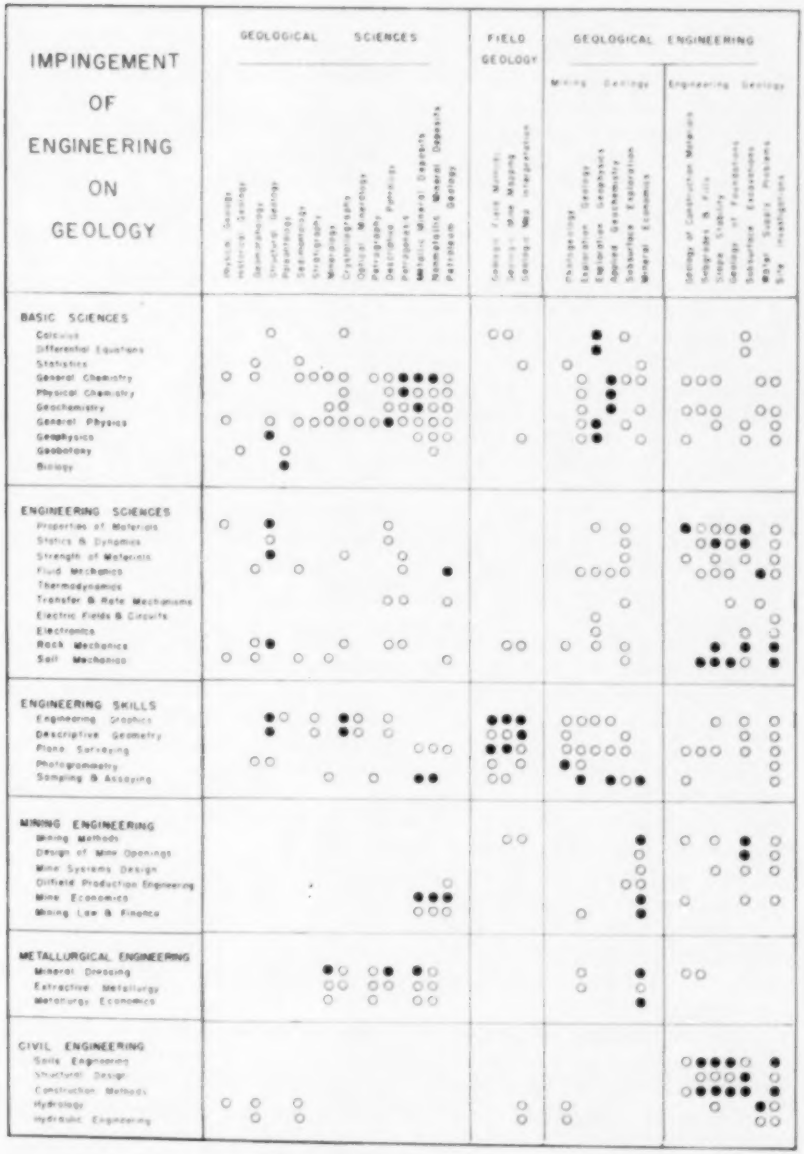


FIG. 1. IMPINGEMENT OF ENGINEERING ON GEOLOGY

## THE IMPINGEMENT OF ENGINEERING ON GEOLOGY

One of the principal objectives of our Committee on the Engineering Content of Geology and Geological Engineering has been to explore the impingement of engineering on the geologic field. It was decided after preliminary discussion to investigate this first in a general way and later in a more detailed manner by scrutinizing typical geological courses as they are now taught with a view to finding out how engineering principles might be incorporated with the geologic subject matter. It was foreseen that this might lead in the future to a better integration of engineering and geology within certain subject areas.

To date, the Committee has completed an analysis of the possible influence of engineering on the principal areas of geology. It is not a final analysis but it may be worthwhile to present the interim results.

The Committee employed a numerical rating system to show how basic sciences and engineering sciences, skills, and fields impinge on the major geologic subdivisions of geological science, field geology, and geological engineering. Each committee member rated the engineering topics shown on the left side of the chart in Figure 1 as to their influence on the geologic subjects across the top of the diagram. The procedure was to evaluate each topic on a "1" to "3" scale: "1" meant that the engineering influence was either non-existent or only of incidental or supplementary value; "2" implied that the engineering aspect was desirable for teaching purposes; and "3" meant that the engineering aspect was indispensable to the adequate teaching of the geologic subject.

The numerical ratings were totalled and averaged, and the results are shown in Figure 1. For graphical presentation, the ratings "1," "2," and "3" are portrayed as blank spaces, open circles, and solid circles, respectively.[4]

The basic sciences are of about equal importance in the geologic fields (Fig. 1). Mathematical training beyond trigonometry and analytic geometry is desirable in several areas; differential equations appear to be of importance only in the field of applied geophysics; an understanding of statistical analysis, including probability theory, is desirable in several geologic areas where quantitative studies are receiving greater attention.

General physics and chemistry are really fundamental to the proper understanding of geologic processes as implied in our rating of these sciences. The related fields of special interest, geophysics and geochemistry, are considered to be necessary in the teaching of petrology and economic geology and to be of great importance in the successful utilization of their field applications in mining geology.

The impingement of engineering sciences and skills also is shown in Figure 1. Knowledge of the nature and properties of materials (as taught by Michigan Tech's Department of Engineering Mechanics) is of moderate importance in physical geology and of prime importance in structural geology

[4] Because the assigned values are the averages of the opinion of many individuals, they do not necessarily represent the authors' opinions. Further, a rating of 3 (indispensable) may refer to only a segment of a subject.

and in descriptive petrology. This engineering science may also be extremely important in the field of engineering geology. Statics and dynamics find their greatest application in certain parts of engineering geology.

Fluid mechanics is fundamental to the proper understanding of the occurrence of petroleum and groundwater, and in the utilization of exploration and recovery techniques for these two resources. Fluid mechanics also is important in understanding the behavior of some soils in construction work as well as in the application of certain techniques of foundation treatment.

Thermodynamics [5] appears to have relatively little bearing in the geological sciences and in geological engineering. Likewise, transfer and rate mechanisms, and (except for application in applied geophysics) electrical theory, fields, and circuits, and electronics have relatively little impingement on geological sciences and geological engineering.

The subjects of rock mechanics and soil mechanics, although not usually included in geologic curricula, appear to have considerably greater importance to geology than some of the foregoing engineering sciences. Their desirable impingement is apparent in both geological science and geological engineering. The growing recognition of this relationship is expected to lead to better coverage of these fields in geological engineering curricula throughout the country.

Engineering graphics and descriptive geometry were classed as engineering skills in this study. Their impingement ranges from supplementary to fundamental importance in most areas of geological science and field geology.

Plane surveying is particularly important in field geology and in geological engineering. Photogrammetry is important in field geology and in geologic interpretation of air photos.

An understanding of sampling and assaying methods and techniques is basic to economic geology and the specialized area of mining geology.

Figure 1 also shows the possible impingement of the mining, metallurgical, and civil engineering fields on the various components of geological science and geological engineering.

Metallurgical engineering subjects impinge at least to some extent on mineralogy, petrology and petrography, economic geology, and on the evaluation of mineral deposits. Their influence is very slight in engineering geology.

Mining engineering and civil engineering impinge very specifically in the geological engineering field wherever knowledge of mining and construction methods is useful, or wherever an understanding of the usage and behavior of natural materials is required, or whenever special economic considerations of an engineering nature enter into a geologic problem.

## THE VALIDITY OF GEOLOGICAL ENGINEERING

The results of the foregoing survey of the impingement of engineering on geology are qualitative rather than quantitative in the true sense. This is

[5] "Thermodynamics" as used here refers to the mechanical engineering treatment of the subject with emphasis on applications of the gas laws to prime movers and other mechanisms. It is understood that the Geological Engineer will gain an adequate knowledge of chemical thermodynamics, kinetics, etc., in physical chemistry and geochemistry courses.

because the Committee's system of rating was an arbitrary one designed for the purpose of presenting its findings in graphic form. Nevertheless, the results clearly show that the understanding of engineering concepts generally is essential for a fully rounded academic program in Geological Engineering. The understanding of engineering principles is to be gained through the study of various engineering sciences and selected subjects in the fields of mining, metallurgical, and civil engineering.

The possible impingement of specific sciences and subjects has been discussed. In summation, it may be stated that knowledge of mathematical and physical sciences is implicit since they form the basis of all well-organized curricula in both Geology and Geological Engineering. The influence of engineering skills is about equally divided in the three geologic subdivisions but the influence of the engineering sciences is greater in geological engineering than it is in geological science. The overall influence of the specialized engineering fields generally is less than is the influence of the engineering sciences and skills, but the impingement of particular engineering subjects is quite marked in geological engineering applications pertaining to mineral exploration and civil engineering construction.

The impingement study suggests that some segments of the engineering sciences might well be deemphasized in Geological Engineering training in favor of other sciences and engineering subjects that appear to be more closely related to geological work. It is especially at this point that the flexibility provided for in ECPD's Additional Criteria should be wisely applied.

The impingement study further demonstrates that there are many points where engineering concepts can and should be integrated into geological subjects in undergraduate courses. Much of this integration has already occurred in the better Geological Engineering curricula. More is possible, and when accomplished will greatly enhance the validity of Geological Engineering. Our definition of the field would then be better realized.

So much for the subject matter and its integration. Let us turn now to another source of misunderstanding. This is the extent to which the concepts and practice of analysis and design enter the Geological Engineering curriculum.

Analysis, broadly speaking, may be taken to mean the definition of a problem, its breakdown into its several parts, and the collection and classification of data for each part. Design picks up the end product of analysis, interprets it in the light of natural law, economics, and other relevant factors, and produces a workable plan.

This sequence of operations is readily understood in the context of planning and designing a bridge, an electrical generating station, or a factory. It is equally applicable to enterprises involving geological engineering, but appears to be less well understood by many engineers not directly concerned. This idea was stressed several years ago in a paper by Shenon (9). An example of geologic analysis and design may help to clarify this point.

*Analysis and Design in Iron Ore Development.*—The successful exploitation of the iron ore deposits of the Labrador-Quebec region by the Hollinger-

Hanna interests was the culmination of nearly a score of years of systematic, large-scale, geologic analysis and design (10).

The Labrador-Quebec region was little known prior to 1930 although A. P. Low of the Geological Survey of Canada reconnoitred parts of the region in 1892–95 and reported iron formation occurrences resembling those of the Lake Superior region. By analogy with the widespread distribution of ores in the Canadian Shield, it was reasoned that the region merited prospecting for various types of metallic and nonmetallic mineral deposits (11).

Space forbids discussion of company formation and organization. It will suffice to state that the Newfoundland Commission of Government granted a prospecting concession of over 20,000 square miles to the Labrador Mining and Exploration Company in 1936. An adjoining concession of 3,900 square miles in New Quebec was acquired in 1941 by Hollinger Consolidated Gold Mines, Limited, which had purchased the Labrador Company. The first Hollinger-controlled exploration commenced in 1942, and in 1942–43 the M. A. Hanna Company joined forces in the project.

Under the terms of the concessions, portions of the area were to be progressively relinquished to the Crown and, therefore, one of the principal problems facing the Hollinger-Hanna technical staff was to plan their geologic exploration to permit judicious rejection of less promising ground. Thus the main purposes of geological work were: "(1) To find and develop enough ore to justify bringing the project into production, and (2) to learn enough about the concessions to permit selection in the time available of the best 500 square miles—from an iron ore stand-point—for sub-leasing" (10).

The complexity of the problem at the start was immense due to a variety of factors including the scarcity of geological information, the non-existence of topographic maps, and the unavailability of aerial photographs. The lack of navigable rivers, roads, and communications imposed further obstacles.

Preliminary efforts were directed to aerial sketching for planning purposes and ground surveying using stadia, range-finder, and compass traverses to provide control for the construction of base maps. These maps were used for geologic reconnaissance mapping of lithology and stratigraphy along plotted traverse lines. Prospectors searched the area for deposits of precious and other metals and they examined the outcropping iron ore. Construction of a regional geologic map based on this early work permitted interpretation of structure and stratigraphy and materially guided later exploration.

Exploration gradually evolved into a systematic pattern under the direction of the permanent geological engineering staff and definite procedures were established for the different phases of the investigations.

The period 1945–1950 was one of concentrated exploration effort directed to the objectives of (1) proving a minimum 400 million tons of direct shipping, open pit, iron ore as a prerequisite to production and (2) eliminating unfavorable parts of the concession areas.

The program of ore development and ground selection was directed by the geological engineering staff. They sited all drill holes, test pits, and test shafts. They logged all the drill core, and also supervised all sampling of drill holes and underground and surface workings. They directed tests to

determine the structure, specific gravity, and moisture content of the ore, and they made field tests to determine volume factors for tonnage calculations. In addition, the geological engineering staff conducted ground geophysical surveys of selected areas. They also set up a photogrammetric section and prepared accurate base maps of all potential iron ore areas, using air photos taken from company aircraft.

Interpretation and evaluation of exploration data were carried on during this period and at an increasing pace until 1952. The detailed geological mapping, metallurgical sampling and testing, and classification of ore resulted in a reserve figure of 418 million tons of direct shipping ore by the end of 1950. Thereafter, some of the staff were diverted to studies of the amenability of marginal ores to beneficiation, and others commenced planning studies for pit layouts, location of treatment plants and railroad loading spurs, and many other design tasks related to the development and production phases of the project.

The achievement of developing this tremendous reserve of iron ore and attaining a current production of around 12 million tons yearly rests firmly on geological engineering. The logistics, deployment, and methodology in concentration upon ore targets and the proving up of world-significant quantities of both direct-shipping and beneficiating iron ores in Labrador-Quebec demonstrate analysis and design of a peculiarly geological engineering nature.

It is doubtful that the geologists involved in these studies were particularly qualified in some of these phases of the mineral industries when they left college and this points up the "practice and experience" components of our definition of Geological Engineering. It further emphasizes the interdependence of ore microscopy and mineral beneficiation, and the interrelationship of economic geology, economics, and engineering.

## CONCLUSIONS

The foregoing discussion leads to several conclusions:

First, the purpose and function of Geological Engineering have been reviewed. There seems to be no doubt that this is indeed a valid field of specialized engineering endeavor within the limits of the mineral industries and the civil engineering construction field.

Second, it was pointed out that this specialized practice necessitates an integration of the geologic sciences and engineering principles during academic training. The impingement study carried on by the Michigan Tech Committee emphasizes this fact, and it shows clearly where the integrational aspects may be best developed.

Third, analysis of the impingement of engineering on geology indicates how a better curriculum in Geological Engineering may be constructed.

Finally, the matter of analysis and design is a critical one in the assessment of the validity of Geological Engineering. There is ample evidence that the geological engineer uses the techniques of engineering analysis and design but the problem is to make this more widely understood.

It is hoped that this paper dealing with an assessment of Geological Engi-

neering in both its professional and academic aspects may generate further discussion that will contribute to the vitality of this engineering field.

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HOUGHTON, MICH.,
*Dec. 11, 1959*

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# SCIENTIFIC COMMUNICATION

## *RADIOACTIVITY OF ALUMINUM METAL*

J. A. S. ADAMS AND K. A. RICHARDSON

During a recent study of the thorium and uranium concentrations in bauxites (2, 5), it was found that in the processing of bauxite, much of the thorium and uranium is concentrated into the red mud, and calcined alumina contains very small amounts of these elements. For this reason, aluminum metal might also be expected to have rather low radioactivity. The radioactivities of a number of aluminum samples were measured by alpha counting, and the results are presented in this paper.

Table 1 gives the gamma ray spectrometer data on Surinam material balance samples. Adams, Richardson, and Templeton (2) give the procedures. These samples, obtained through the courtesy of the Aluminum Company of America, consist of Surinam bauxite, calcined alumina, red mud, and classifier sand, from the East St. Louis alumina plant. Some of the gamma ray determinations were verified by chemical analyses, indicating that the thorium and uranium are in equilibrium with their daughter products in the bauxite and red mud samples. The results in Table 1 show that more than 80 percent of the thorium and uranium in the bauxite is concentrated in the red mud, and less than 5 percent of these elements is extracted with the alumina. The calcined alumina contains 4.9 ppm of thorium and 0.3 ppm of uranium, and has an alpha activity of 0.054 counts per hour per square centimeter. A sample of alumina produced from Arkansas bauxite has an alpha activity of 0.039 counts per hour per square centimeter. These alpha activities were measured a few weeks after the alumina was produced. Counting of the same samples approximately two years later indicated an increase in activity of approximately 100 percent, but this apparent change may have no statistical significance.

The alpha counting technique that was used in this study is the same as that described by Adams, Richardson and Templeton (2). The powdered material balance samples were counted in a 2 inch diameter planchet with a depth of $\frac{1}{8}$ inch. The alpha activities of the aluminum samples were measured on metal discs of the same diameter and thickness as the planchets.

The metal samples that were studied included 7 modern aluminum samples in varying degrees of purity, 3 samples of aluminum produced 30 to 40 years ago, and three National Bureau of Standards aluminum alloy samples. The alpha activities of the samples are listed in Table 2, with more detailed sample descriptions. The statistical error in these low level measurements ranges approximately from $\pm 20$ to $\pm 90$ percent of the measured activity.

TABLE 1

THORIUM AND URANIUM DATA ON SURINAM MATERIAL BALANCE

| Sample | Weight, lbs | Th, ppm | U, ppm | Alpha* activity | % Th | % U |
|---|---|---|---|---|---|---|
| Bauxite | 1.9 | 74.2 | 3.6 | 16.8 | | |
| Calcined alumina | 1.0 | 4.9 | 0.3 | 0.054 | 3.5 | 5 |
| Fine red mud | 0.48 | 281 | 11.6 | 65.6 | 96 | 82 |
| Classifier sand | 0.05 | 122 | 10.1 | 31.0 | 4.3 | 7.4 |

* Alpha activities in counts per hour per square cm.

The average alpha activity of the seven relatively recently produced metal samples, KR-45 to KR-51, is 0.089 counts per hour per square centimeter. Measurement of the activities of these samples two years before the counts listed in Table 2 were made gave an average value twice as great. However, the activity of the metal being only slightly above background, its apparent decrease is within statistical limits of error.

The gradational decrease in purity in the series of samples KR-46 through KR-51 does not cause a change, within statistical limits of error, in the radioactivities of the samples. A sample taken from an anode of the electrolytic aluminum purification process has a measured alpha activity of 4.3 counts per hour per square centimeter. This is approximately the activity that would be expected for a sample containing 5 to 10 ppm of thorium and

TABLE 2

ALPHA ACTIVITY OF ALUMINUM METAL SAMPLES

| Sample number | Alpha activity | Sample description |
|---|---|---|
| KR-39 | 0.13<br>0.16 | N.B.S. #601: 4.38% Cu, 0.39% Mg, 0.88% Si, 0.52% Fe, 0.81% Mn, 0.020% Cr, 0.015% Ti. |
| KR-40 | 0.16<br>0.18 | N.B.S. #602: 4.44% Cu, 1.49% Mg, 0.130% Si, 0.28% Fe, 0.63% Mn, 0.007% Cr, 0.012% Ti. |
| KR-41 | 0.34<br>0.33 | N.B.S. #603: 0.29% Cu, 1.01% Mg, 0.52% Si, 0.21% Fe, 0.24% Cr, 0.037% Ti. |
| KR-42 | 0.79<br>0.69 | Aluminum produced from Arkansas bauxite in 1918. |
| KR-43 | 0.41<br>0.24 | Aluminum produced from Arkansas bauxite in 1920. |
| KR-44 | 0.24 | Aluminum produced from French or Irish bauxite in 1907. |
| KR-45 | 0.074 | Aluminum produced recently from Surinam bauxite. |
| KR-46 | 0.089 | Aluminum samples KR-46 to KR-51 are produced from Arkansas bauxite. This series grades from 99.9% purity in KR-46 to 94% in KR-51. KR-48 has the composition typical of modern aluminum. |
| KR-47 | 0.14 | |
| KR-48 | 0.069 | |
| KR-49 | 0.11 | |
| KR-50 | 0.059 | |
| KR-51 | 0.089 | |

* Alpha activities in counts per hour per sq cm from solid metal surface.

uranium. Gamma ray spectral analysis of this sample indicates concentrations of less than 1 ppm for both of these elements. The radioactive decay series must, then, be out of equilibrium. Because the sample is over two years old, the alpha activity must be due to a concentration of some of the longer-lived nuclides.

The National Bureau of Standards samples, KR-39, KR-40, and KR-41, containing 93 to 98 percent aluminum (see chemical analyses in Table 2),

TABLE 3

ALPHA ACTIVITIES OF SOME METALS

| Material | Alpha counts per hour per 100 cm² |
|---|---|
| Steel (commercial) | 3 |
| Brass (commercial) | 5 |
| Copper (commercial) | 9 |
| Aluminum (commercial) | 31 |
| Tin (commercial) | 121 |

exhibit alpha activities somewhat greater than the samples of modern aluminum. Probably the increased radioactive content was added to these alloys with one or more of their minor metal constituents.

The three old aluminum samples, KR-42, KR-43, and KR-44, are two to eight times more active than the modern samples. This might be due to a greater radioactive impurity in the samples at the time of production, or to a build-up of radioactive daughters from a non-equilibrium condition.

TABLE 4

BETA ACTIVITIES OF SOME METALS

| Material | Beta counts per minute per 100 cm² |
|---|---|
| Copper tubing | 0.05 |
| Brass rod | 2 |
| Steel scale | 5 |
| Aluminum (2S) | 6 |
| Aluminum (superpure) | 4 |
| Lead (modern) | 11 |
| Lead (16th century) | 1 |

Bearden (3) measured the alpha activities of materials commonly used in the construction of radiometric equipment, and some of these are listed in Table 3. Table 4 gives more recent measurements (4) of the beta activities of some metals. These data show that, although aluminum is produced from an ore with relatively high radioactivity, the radioactivity of aluminum metal is comparable with that of other common metals.

ACKNOWLEDGMENT

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THE RICE INSTITUTE,
HOUSTON, TEXAS,
*April 23, 1960*

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# DISCUSSIONS

## *ALTERATION OF ILMENITE*

*Sir:* During the last three years there have appeared in Economic Geology several interesting papers and discussions (1–9) dealing with alteration of ilmenite, some of which tend to confuse the terminology, or give a misleading impression of the nature of altered ilmenite and other titaniferous materials. Some of the methods used and materials studied were quite similar to those described in a paper of which the writer was a co-author (10), and which Bailey, Cameron, Spedden, and Weege (1) very kindly described as being "noteworthy because for the first time, the results of chemical, X-ray and magnetic concentration studies are correlated with study of opaque minerals of beach sands in polish surfaces."

In his paper on alteration of Malayan ilmenite, Flinter (4) states that ". . . the Malayan material was similar to the material described by Overholt et al. . . ." Flinter's results show that the alteration present in Malayan ilmenite is also very similar to that which we described for ilmenites from India, Brazil, Florida, and North Carolina. He may therefore find our 1954 paper of some interest in the event that he has not yet seen it.

Regarding Flinter's suggested use of the term, "hydroilmenite," for a partially altered ilmenite, the writer prefers to call such material simply "altered ilmenite" or "weathered ilmenite," since the chemical and mineralogical composition varies with the degree of alteration, and the amount of water present is very small. The use of an additional term would more than likely only add to the confusion which has existed regarding the nature of the titanium minerals present in sand deposits.

Flinter's proposed use of the term, "arizonite," for fine grained but well crystallized alteration products of ilmenite, seems quite unjustified, because this type of material is well covered by the term "leucoxene," which is in common use, especially for the high-$TiO_2$ portions of commercial concentrates. Since the term, "arizonite," was originally proposed for the hypothetical compound $Fe_2O_3 \cdot 3TiO_2$, its continued application to mixtures of finely crystalline $TiO_2$ and iron oxides in beach sands is misleading.

In their paper "An X-ray Study of Leucoxene from Quilon, India," Karkhanavala, Momin, and Rege (5) state that in our 1954 paper we "showed that the Quilon concentrate consisted of ilmenite, hematite, and rutile only, (and) concluded that *all* the non-ilmenite portion of the concentrate consisted of a porous mixture of fine grained rutile and iron oxide formed as a result of alteration of ilmenite." It was not intended to give the impression that ilmenite, hematite, and rutile were the only compounds present,

although X-ray analysis detected only these phases. It was stated that "*nearly* all the non-ilmenite portion . . . consisted of . . . fine grained rutile and iron oxide . . .," and indicated that Quilon, Florida, and Brazilian ilmenites contain smaller amounts of crystalline components than does unaltered ilmenite. X-ray patterns further indicated that the dominant minerals in the sand ilmenite concentrates approach a size range amorphous to X-rays, that is, crystallite diameters in the order of 50 to 100A. It was therefore shown that some of the alteration products were amorphous, or nearly so.

In their study of alteration of ilmenite at 650° and 850° C, Karkhanavala and Momin (6) used as their standard ilmenite the commercial ilmenite concentrate produced at Quilon. It should be pointed out that Quilon ilmenite is already rather extensively altered, so that the results obtained on this material should not be taken as directly applicable to fresh, unaltered ilmenite. Unless the "commercial grade 1 concentrate" used is very different from the Quilon ilmenite that the writer has examined, its chemical analysis alone would indicate that it is too high in $TiO_2$—around 59 percent—to be suitable for investigating the behavior of pure ilmenite. It is rather surprising that no results of chemical analysis, of either the starting material or the oxidation products, were reported. It might be interesting to check how the chemical analyses of "brown leucoxene" and the 850° oxidation product compare with the average composition postulated for these materials ($1Fe_2O_3$-$5Fe_2O_3 \cdot TiO_2$-$7TiO_2$).

In a paper on "arizonite," Karkhanavala (7) disagrees with other investigators who concluded that "arizonite" is a mixture of anatase, rutile, and hematite. Arguments are presented to support the view that "arizonite" is actually a crystalline form of the compound $Fe_2O_3 \cdot 3TiO_2$, as originally believed by Palmer.

Karkhanavala's conclusions are based on what he describes as "limited success in synthesizing arizonite under hydrothermal conditions" (as a mixture with hematite and anatase), on deviations of the relative intensities of X-ray diffraction lines in natural "arizonite" from those of standard A.S.T.M. patterns for anatase, hematite, and rutile, and on slight differences in the d-spacings of the hematite lines. The X-ray pattern of the synthetic product indicates that it consisted in part of material resembling natural "arizonite." Although the X-ray diffraction pattern shows lines corresponding to rutile, Karkhanavala claims that the formation of rutile under his experimental conditions (300° C, 1200 psi) is impossible. However, there is general agreement among other investigators that rutile can form at low temperatures. For example, Gruner (8) found that ilmenite alters to rutile and pyrite at 300° C in a dry stream of $H_2S$. Hartman (9) in a recent paper reviews the factors controlling formation of $TiO_2$ polymorphs, making it clear that rutile has formed at low temperatures in bauxite deposits. Results of a study soon to be published (11) show that rutile was present in synthetic alteration products made from ilmenite at 45–50° C. Karkhanavala's interpretation of his X-ray data is therefore based on a false assumption. In any case, since his synthetic product was admittedly a mixture, there is no

way of determining accurately the chemical composition of the phase claimed to be "arizonite."

Variations in relative intensities of X-ray diffraction lines with changes in particle size, shape, and orientation are not unusual, nor are variations in d-spacings when impurities are present. The correspondence of the arrangement of the diffraction lines of natural "arizonite" to those of a mixture of anatase, rutile, and hematite seems too close to be dismissed as coincidental.

If a pure compound $Fe_2O_3 \cdot 3TiO_2$ could be prepared hydrothermally, or by any other means for that matter, even this would not prove that natural "arizonite" consists of such a compound. The X-ray data would still be subject to interpretation as to what compounds were present. However, until a pure compound can be prepared, containing only one phase, from which a standard X-ray pattern can be obtained, there is no logical basis for interpreting the natural "arizonite" X-ray pattern as other than a fine grained mixture of oxides of iron and titanium.

In 1956, Bailey, Cameron, Spedden, and Weege (1) described a study of altered ilmenites from Mozambique, Ceylon, Brazil, and Florida. They concluded that alteration proceeds in three rather distinct stages. In the first stage, "patchy ilmenite," ilmenite grains alter to patchy intergrowths of ilmenite and an isotropic substance (amorphous iron-titanium oxide), of lighter color than ilmenite. The second stage is reached when a grain has been completely transformed to the isotropic material. The third stage involves progressive alteration of the isotropic substance to crystalline leucoxene. It was pointed out, however, that brown leucoxene is not sharply distinct from amorphous iron-titanium oxide.

During a study of the mechanism of alteration of ilmenite (11), the writer observed in slightly altered ilmenite grains from North Carolina sands a small mount of a homogeneous gray alteration product that occurs along cracks and twin lamellae. This material is a little darker in color than fresh ilmenite and in some areas contains a little crystalline leucoxene. This dark material may correspond to what Bailey et al. call iron-titanium oxide, or Stage 1 alteration, although the color is different. This sort of material was also observed in association with granular, anistropic alteration products (leucoxene) in New Jersey ilmenite.

The products described in our 1954 paper displayed gradational, rather than sharply defined stages of alteration. Altered areas appeared gray, porous, and finely granular, the porosity, grain size, and intensity of internal reflection in polarized light increasing gradually with the degree of alteration. Some of the patterns of alteration were "patchy," but were not limited to the very early stage of alteration.

In discussing parts of this paper (10), Bailey et al. express uncertainty as to whether some of the materials we studied were ilmenite concentrates or total heavy mineral concentrates (1, p. 265). As indicated in the title of Table II, "Chemical Composition of Various Ilmenite Concentrates," they were actually ilmenite concentrates. In discussing chemical and magnetic data (1, p. 270), Bailey et al. make the following statement: "Lynd and his coworkers concluded that the beach sands they studied showed various degrees

of alteration of ilmenite, the alteration involving leaching of $TiO_2$, . . ." This is not true. *We concluded that leaching of iron is involved,* so that the alteration products are enriched in $TiO_2$.

It is certainly true, as Bailey et al. point out (1), that the relationship between chemical composition and magnetic behavior of altered ilmenites is poorly understood. Fractions obtained from ilmenites of different localities by magnetic separation at the same amperage often show wide variation in chemical composition. The writer agrees that further investigation of the chemistry of alteration is needed, and it would help considerably if chemical analyses of the materials worked with and the products obtained could be included in papers on the subject. It is difficult to compare the results of different studies, when, as in the paper of Bailey et al., analyses are reported for only one set of three magnetic subfractions, with no indication of distribution of iron content between $Fe^{2+}$ and $Fe^{3+}$, or as in two papers of Karkhanavala et al., (5, 6) no chemical analyses are given.

Regarding the term "leucoxene," Allen (2) emphasizes the advisability of retaining this term for the alteration products, whether crystalline or amorphous, in which titania occurs in rocks. Bailey and Cameron (3) agree with this usage when differentiation of the individual components in alteration products is difficult or impossible, but in describing beach sands where "amorphous iron-titanium oxide" could be distinguished from crystalline leucoxene, they prefer to reserve the term "leucoxene" for alteration products containing finely crystalline $TiO_2$. They repeatedly refer to "leucoxene" as finely crystalline $TiO_2$, which they say "carries 75 to 92 pct $TiO_2$," but would probably agree that even crystalline leucoxene contains iron oxide and other impurities, and that the term "leucoxene" should be used to cover the whole mixture of alteration products, and not just one component of it. If the term "leucoxene" is acceptable for crystalline mixtures of iron and titanium oxides, it should also be acceptable for amorphous mixtures of these oxides, wherever they occur. If desired, the degree of crystallinity of the alteration products could be satisfactorily indicated by such phrases as: amorphous leucoxene, partially crystalline leucoxene, or crystalline leucoxene. Because of the gradational nature of the changes brought about by alteration, it seems somewhat misleading to use terms such as Stage 1, which imply that alteration generally proceeds in well-defined, consecutive stages.

In conclusion, the following recommendations are made regarding the terminology used and information given in describing work on alteration of titanium minerals.

1. Chemical analyses should be given, at least for $TiO_2$, FeO and $Fe_2O_3$, on all titaniferous materials studied.

2. The term "ilmenite" should be qualified by the use of an appropriate adjective—e.g. *weathered* ilmenite, when describing Quilon ilmenite—when it applies to a material other than substantially unaltered, pure ilmenite. Chemical analyses should be used to indicate the degree of purity.

3. The introduction of new terms, or the revival of old, little known, or discredited terms to designate alteration products of titanium minerals is

unjustified, and should be avoided, since all of these materials can be covered by the term, "leucoxene," which is in current use.

4. The term, "leucoxene," should continue to be used as a general name for alteration products containing titania. Where different types of leucoxene are recognizable, one or two descriptive adjectives can be used to indicate the nature of the alteration products: whether crystalline or amorphous; gray, brown or white; and if crystalline, whether the titania is present as anatase, rutile, brookite, perovskite, or sphene.

5. It is suggested that the Committee on Publications of the Society of Economic Geologists review the various proposals which have been made regarding the nomenclature of alteration products containing titania, and recommend a uniform system of terminology.

LANGTRY E. LYND

NATIONAL LEAD CO.,
SOUTH AMBOY, N. J.,
*March 26, 1960*

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## *MALAYAN ILMENITE VS. ARIZONITE*

*Sir:* Dr. Karkhanavala's communication concerning my paper "The Alteration of Malayan Ilmenite Grains and the Question of 'Arizonite'" objects to my suggestion that the term "arizonite" be retained to indicate the third phase of alteration (recrystallization) of ilmenite on the grounds that arizonite is a valid species, representing a finite chemical compound, ferric metatitanate, and states that the term leucoxene is considered a generic name for such alteration products.

I suggested that "arizonite" should be retained to indicate the recrystallized mixed phases of iron and titanium oxides because (a) I felt it was desirable to distinguish between the amorphous stage, (my hydroilmenite), and the

recrystallized stage of ilmenite alteration; (b) I was sufficiently convinced by Overholt et al. ("The Nature of 'Arizonite'," Am. Min., Vol. 35, p. 117–9) that Palmer's original arizonite is in fact such a mixture and (c) it is not only logical, but quite acceptable, to apply the name given by Palmer to material which is similar both in its general chemical composition and X-ray powder pattern, even though it might have been his intention to apply it only to a definite mineral species. Karkhanavala has done nothing to nullify these reasons. He dismisses Overholt's contention that the X-ray data of the original arizonite can be interpreted as a "mixture of hematite, ilmenite, anatase, and rutile." The fact that ilmenite lines are lacking (cf. my paper, p. 727), does not invalidate their conclusion that the original arizonite is a mixture of iron and titanium oxides derived from the alteration of ilmenite. As indicated in my paper the ilmenite structure must necessarily be destroyed first, giving the amorphous hydroilmenite stage, before further recrystallization occurs. Karkhanavala ("The Nature of Arizonite," Econ. Geol., Vol. 54, 1959 pp. 1302–8) dismisses Overholt's interpretation on the basis of certain minor discrepancies (in the X-ray powder pattern) which Overholt et al. considered insignificant but Karkhanavala prefers to consider real. The two factors he chooses are the discrepant intensity values of the subsidiary hematite and rutile phases and the presence of a 2.66 A.U. line. His sole justification for a valid mineral species (i.e. the presence of a 2.66 A.U. line) is much more open to uncertainty. Further doubt is cast by the real difference (p. 1304) in the value of the d-spacing of the most intense line between Palmer's original "arizonite" (d = 3.50) and the photographic and G.M. counter values of Karkhanavala's synthesized material (d = 1.683 and d = 2.69 respectively). The different intensity values between the photographic and G.M. counter results (on the same sample) indicate that little reliance should be placed on any of the absolute intensity values, (this being his first objection). Further, comparison of the original "arizonite" pattern and the G.M. counter pattern does not support the view that $Fe_2O_3 \cdot 3TiO_2$ and Palmer's arizonite are a single unique mineral species but, on the contrary, it supports the "mixture" contention—the arizonite having anatase (strongest line, d = 3.51) as the major phase and the synthetic $Fe_2O_3 \cdot 3TiO_2$ sample having hematite (strongest line, d = 2.69) as the major phase.

Although leucoxene has been used by various workers in connexion with the alteration products of ilmenite, this usage is incorrect and the term cannot be considered a generic name for such alteration products. Despite its various interpretations (and there are numerous papers to testify to them) there is general agreement that it is mainly amorphous $TiO_2$ plus varying amounts of crystalline phases of rutile, anatase, and/or brookite. i.e. it is pure $TiO_2$. It contains no iron oxide, which is a fundamental component of the end-product of ilmenite alteration. Furthermore, use of the term implies derivation from rutile, brookite, anatase, sphene or similar mineral, whereas use of the term arizonite (or whatever is adopted) should, by definition, imply derivation from ilmenite.

Summing up, I should say that there is no evidence that a valid mineral species having a definite chemical composition of $Fe_2O_3 \cdot 3TiO_2$ and a dis-

tinctive X-ray pattern does exist. Even if it does exist, however, it is not simliar to the original material called "arizonite" by Palmer. Palmer's arizonite is almost certainly a mixture of iron and titanium oxides present as various crystalline phases. This is exactly similar to the final recrystalled stage of alternation of an ilmenite and therefore it is acceptable to refer to this stage as "arizonite." If this is undesirable, the term "hydroilmenite" should be extended to cover both the amporphous and recrystallized stages of an altered ilmenite, the terms "amorphous" and "recrystallized" being used as appropriate. On no account can the term "leucoxene" be applied. Whatever term is used, it would have a specific significance—a variable mixture of iron and titanium oxides (either amorphous and crystalline or crystalline only) derived by the alteration of ilmenite.

His statement that there is no evidence to support my suggestion regarding pseudobrookite is, I feel, a misunderstanding that would not have arisen had there been a comma between "unstable" and "high-temperature" in line 37, page 727, of my paper. I meant to suggest that pseudobrookite, formed at high-temperature (e.g. 1,100° C in my sample) is probably unstable at lower temperatures, and might revert to a mixture of hematite and anatase. I note that this is what Overholt et al. state (end of paragraph 2), but I did not have access to their paper until very recently. The instability of pseudobrookite at lower temperatures (below about 950° C) is well shown by MacChesney & Muan's excellent study of the iron oxide-titanium oxide system (Am. Min. Vol. 44, Sept.-Oct. 1959, pp. 926–945).

In conclusion, I cannot agree with Karkhanavala's explanation of the abundant co-occurrence of pseudobrookite and altered ilmenite found by him in the Quilon sands. The answer must surely be that primary pseudobrookite occurs in the source area.

B. H. FLINTER

GEOLOGICAL SURVEY OF MALAYA,
IPOH, MALAYA.
*March 24, 1960*

## *SULFIDE OREBODIES AT YAURICOCHA, PERU*

*Sir:* I would like to comment on H. Ward's recent article (ECON. GEOL., Vol. 54, p. 1365–1379).

While Ward puts forward an interesting idea to explain the textures shown by the pyrite he fails to substantiate it. The distribution of the breccias associated with mineralization, both in time and space, and their relationship to the regional joints and fractures precludes their being reef breccias. Banding that occurs in both hard and soft pyrite shows a shape and distribution that is completely incompatible with the replacement of an organic reef. I hope to publish a different hypothesis in the future showing that the emplacement of the orebodies was accompanied by mineralization stoping.

D. R. S. THOMSON

ROYAL SCHOOL OF MINES,
LONDON, S. W. 7.
*Mar. 25, 1960*

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# REVIEWS

**Shlikhovaya S'emka i Analiz Shlikhov.** (Alluvial prospecting and the analysis of heavy concentrates.) By I. M. Ozerov. Pp. 379, Figs. 140. Gostoptekhizdat, Moscow, 1959. Price, 11r. 10k.

Alluvial prospecting for gold was for centuries a widespread occupation throughout the territories of the Tsars, and the Russian term *shlikh*, meaning a heavy mineral concentration produced by panning, has a currency unparalleled by any comparable word in English. The Uralian platinum, the Kolyman gold, the Yakutian diamonds were all first recognized in *shlikhi*. A modern Russian textbook on the principles, methods and techniques of alluvial prospecting therefore promised to be of outstanding interest, and certainly there is much of practical value that can be learned from this unusual work by Dr. Ozerov. After some general chapters on the weathering of rocks and ore deposits, on the transport and deposition of heavy minerals, and on correlation by heavy mineral analyses, the manual goes on to discuss field methods of alluvial prospecting and the various laboratory techniques whereby heavy minerals may be specifically identified. The section on microchemical tests on heavy grains is good and there are long tabulations of such minerals classified according to various physical properties. But in some respects the work is simultaneously disappointing and illuminating. Apparently the Russian laboratories have no instrument like the Frantz isodynamic separator; and electrostatic separation, so widely used in some Western laboratories, is not mentioned at all. Uraninite is listed 13 times in the index—but 12 of these mentions relate solely to the physical properties of this mineral (as specified in any good mineralogical textbook) and the sole textual reference confines itself to the bald statement that "In concentrates uraninite is of rare occurrence." An important omission (perhaps of no significance in Russian climates) is gorceixite, which is derived from lateritized carbonatites and which so often accompanies alluvial diamonds in tropical terrains.

C. F. Davidson

University of St. Andrews,
Scotland,
*May 6, 1960*

**Beaches and Coasts.** By Cuchlaine A. M. King. Pp. 403; figs. 149. St. Martin's Press, Inc., New York, 1960. Price, $14.50.

C. A. M. King, who is a British geographer, has developed an outstanding reference work in this book about shore processes and their products. His treatise is based largely upon the numerous quantitative studies of more recent years, representative chapter headings being: "Beach Profiles—Experimental Results and Surveying Techniques" and "Methods of Research" (including sections devoted to theoretical, experimental, and field methods). In all, there are eight chapters about shore processes and four on the resulting beach and coastal forms.

The chapter dealing with classification of coasts includes an appraisal of the classifications advanced by Johnson, Shepard, Cotton, and Valentin. King favors the descriptive classification of Valentin, because it provides a solution to the problems of frequent and rapid changes of sea level, geologically speaking. It is important also, from a practical standpoint, to make Valentin's distinction between coasts that are "advancing" and those that are "retreating," as these two types constitute very different problems for the coastal engineer. There is little doubt that both geologist and coastal engineer will find this a basic reference work for some time to come.

W. Harrison

Dartmouth College,
Hanover, N. H.

**Geological Nomenclature (1959).** Edited by A. A. G. Schieferdecker. Published by the Royal Geological and Mining Society of the Netherlands. Goringhem, Holland. 11.-US.

At the same time a glossary and a dictionary, this volume contains 5489 items with almost no duplications. The listing is arranged with the English term and definition first, followed by the Dutch, the French, and the German equivalent terms or phrases.

The first part (p. 1–350) contains the terms and definitions in English followed by the translations of the terms only. This organization is according to fields of geology. The second part (p. 351–519) is an alphabetical list of all the terms defined and translated in the first part.

The individual fields are: Geomorphology (1,386 terms, including weathering; ground-water hydrology; speleology; rivers; lakes; swamps, marshes, moors; glaciology; oceanography; coasts and islands, reefs); Genetic Physiography (585 terms); Sedimentology (434 terms); Stratigraphy (423 terms); Tectonic Geology (515 terms); Geophysics (369 terms); Vulcanology (821 terms); Orogenesis (145 terms); Mineral Deposits (334 terms); Petrology of Igneous and Metamorphic Rocks (469 terms).

As an example of the subdivision of the individual fields the one on mineral deposits may be listed. It contains: I. General terms. II. Structure and shape of mineral deposits. III. Orientation of mineral deposits. IV. Distribution of values in mineral deposits. V. Processes of formation of mineral deposits. VI. Hypogene rock alterations. VII. Supergene rock alterations. VIII. Cosmo- and geochemistry. IX. Classification of mineral deposits. X. Textures and structures of ore minerals. XI. Various mineral terms. This well organized grouping may serve as a guide in repeating or brushing up the basic principles of economic geology. The editors of this section are: J. Westerveld, University of Amsterdam; E. Raguin, École Nat. Supérieure des Mines, Paris; and Paul Ramdohr, University of Heidelberg.

A close examination of the quality of the definitions has revealed that, if compared with the little space used, the definitions are accurate and remarkably free of dogmatic concepts. The printing is clear and virtually no errors could be detected. This new dictionary and glossary can be highly recommended to all geologists as a valuable complementary addition to the A C I Glossary.

G. C. Amstutz

Missouri School of Mines
and Metallurgy,
Rolla, Missouri

**International Tin Council, Statistical Year Book 1959.** Pp. 283. International Tin Council, London, 1959. Price, £2-10-0.

This is the first Year Book published by the International Tin Council. It follows the four previous Year Books prepared by the International Tin Study Group, the last of which was issued four years ago. This volume, however, is larger and more complete than the previous ones. It has the same world-wide scope as before.

The volume has two parts. The first deals with tin and tin plate, and the second with the chief users of tin—the canning industry. Each section covers the world, country by country. In the first section is included something of the historical background, the deposits, mining, metallurgy, marketing, and detailed statistics of production of tin, alloys, tin plate, manufacturing and exports. Four general chapters discuss the International Tin Agreement, world tin position since World War II, and the tin trade of the U.S.S.R., China and Eastern Europe.

As before, it is an invaluable reference book.

**Gemstones of North America.** By JOHN SINKANKAS. Pp. 675; figs. 176. D. Van Nostrand Co., Inc., New York, 1959. Price, $15.00.

This large handsome volume emanates from the pen of a U. S. Navy captain and a noted gemologist, for the use of the student; the collector and connoisseur of gems; museums; and jewelers. It brings together in a single volume a wealth of information about gemstones in North America, their properties, appearance, and where and in what quantity and quality they occur.

The first chapter acquaints the reader with the properties and features that make gemstones objects of beauty and acquaints him with terminology, crystals, geometry of crystals, crystal growth, cleavage, specific gravity, color, and optical effects. The six succeeding chapters deal with six groups of gemstones, i.e.—principal ones (precious stones), important gemstones, quartz family gemstones, rare and unusual gemstones, massive and decorative gemstones (including many rocks), and organic gemstones, such as pearls and shell, coral, amber, jet, and anthracite coal.

Each of the important stones are fully described, along with the geology and and mineralogy of the deposits, their mode of occurrence, localities and history. Numerous drawings and photos of stones and their occurrence are included. Also, there are several beautiful colored plates of striking gemstones. Four appendices give bibliography (13 p.); a glossary of mineral, rock, and geologic terms (18 p.); a tabular review of gemstone deposits; and a geographic and locality index, as well as a general index.

The volume is a storehouse of authoritative information for anyone interested in gemstones, and a very convenient reference book.

**Minerals of New Mexico, 2nd Edition.** By STUART A. NORTHROP. Pp. 665. Univ. of New Mexico Press, Albuquerque, New Mexico, 1959. Price, $10.00.

This edition is about twice as large as its predecessor and is packed full of information about minerals of New Mexico, as well as knowledge about minerals in general. In Part I, pages 5–80, is a fascinating account under "Highlights in the History of New Mexico Mineralogy and Mining" of the history of the state from prehistoric times through Spanish, Mexican, and American exploration and mining and utilization of minerals. There is included lists of museum specimens,

fluorescent and radioactive minerals, and mineral analyses. This interesting section is followed by one on the "Economic Aspects of New Mexico Mineral Industry" in which is given a general survey and comparisons with other states, changes in trends of exploration and production statistics.

Part II, pages 95 to 568, covers descriptions and records of occurrences. Part III is a list of districts and mining camps; followed by an extensive bibliography. The occurrences are alphabetically arranged from acmite to zoisite, and cross referenced. Information is given regarding localities, occurrences, analyses, history and mining. Of particular interest is Turquois (16 pages) which covers name derivation, occurrence, bibliography, analyses, production, prehistoric mining, archeology, early Spanish explorers, and technology.

This book is of much wider interest than of New Mexico alone, since there is interwoven history, geology, and mining; and it is also a textbook on mineralogy.

**Die Uran-und Goldlagerstätten-Witwatersrand-Blind River-Dominion Reef-Serra de Jacobina: Erzmikroskopische Untersuchungen und ein Geologischer Vergleich.** By PAUL RAMDOHR. Pp. 35; pl. 19. Akademie-Verlag, Berlin. Price, DM10.

Dr. Ramdohr makes a comparative study of the uranium-gold occurrences of these four districts, particularly with respect to a microscopic examination of the opaque minerals present. In the Rand ores he describes gold, pyrite, arsenopyrite, pyrrhotite, chalcopyrite, "uranpecherz," brannerite, carbonaceous material, chromite, magnetite, zircon, spinel, garnet, galena, sphalerite cubanite, and vallerite. He considers there are several kinds of pyrite, one of which he calls pyrite pebbles, which he considers is detrital, being deposited along with the quartz pebbles. Other pyrite is considered to be authigenic. He also considers that the uranium mineral is detrital.

Generally similar mineralogy is described from the Dominion Reef, with the addition of allogenic molybdenite, tantalite, and cobalt minerals. Similar conclusions are drawn.

The Blind River deposits are described briefly. The author considers the following minerals to be allogenic: pyrite, urananite, brannerite, molybdenite, chromite, zircon and monozite. Also included are magnetite, chalcopyrite, galena, gold, cubanite, and bismuth. As authigenic minerals he recognized pyrite, rutile, brannerite, uraninite, magnetite, marcasite, chalcopyrite, sphalerite, galena, vallerite, gold. He considers the uranium minerals and pyrite (in part) to be detrital.

Generally similar minerals are noted for Serra de Jacobina.

He concludes that the uranium minerals, gold, and the pyrite were originally detrital but suffered some working over.

There is also a section on a criticism of C. F. Davidson's ideas that uraninite could not be detrital. Ramdohr believes it is.

The 19 plates contain beautiful photomicrographs of polished surfaces of ores.

**Stratigraphy of the Pre-Simpson Paleozoic Subsurface Rocks of Texas and Southeast New Mexico.** By VIRGIL E. BARNES and others. Pp. 837; figs. 38; pls. 65. Bureau of Economic Geology, The University of Texas, Austin, Texas, 1960. Price, $7.75.

This publication consists of two volumes of text and one of charts, enclosed in a box. It results from a project proposed by the Humble Oil Co. and financed by

Humble, Atlantic, Gulf, Shell, Sun, and Texaco Oil Companies. Other companies and the U. S. Geological Survey contributed by supplying samples, maps, and information. The section includes all sedimentary rocks in Texas and S.E. New Mexico, from the top of the Precambrian to the base of the Middle Ordovician. Its chief purpose was to determine if established or other units of the pre-Simpson sequence could be recognized in the subsurface, and if methods could be found by which these units could be recognized. Dr. Barnes was the main contributor and organizer, but there are additional papers by P. E. Cloud, Jr., A. R. Palmer, E. J. Tynan, R. L. Folk, and E. O. Jones.

Part I of Volume I, by Dr. Barnes, covers the general stratigraphy, correlation, genesis, structures, and thermometry. Part II includes the individual reports of the other authors, as well as several chapters by Dr. Barnes, treating of such fields as paleontological data, insoluble fossils, petrography, clay minerals, chemical phases of isotope ages, thermoluminescence, color, and insoluble residues. Volume II is made up of 11 appendices describing cores, structure and solution phenomena, anhydrite, petrographic descriptions, spectrochemical and chemical analyses, glow curves, and insoluble residue data.

The work is monumental and recalls a previous monographic work, Bulletin 3401, on the structural and economic geology of Texas. It will be of great interest to students and teachers of stratigraphy, and to all petroleum geologists.

## BOOKS RECEIVED

JOHN E. COTTON AND ROGER L. AMES

**Introduction to Solids.** LEONID V. AZÁROFF. Pp. 460. Price, $9.50. McGraw-Hill Book Co., New York, 1960. *Uses crystallinity of solids as a framework for discussing their natu.e and properties; treats of metals, semiconductors and insulators; much good crystallography. Excellent treatise.*

**Invertebrate Paleontology.** WILLIAM H. EASTON. Pp. 701; heavily illustrated. Price, $10.00. Harper & Bros., New York, 1960. *A book for the professional geologist stressing the functional approach to invertebrate paleontology and to evolutionary progression; systematic treatment of orders. Well illustrated. Excellent reference book.*

**A French-English Vocabulary in Geology and Physical Geography.** G. M. DAVIS. Pp. 140. John Mann, London, 1960. Price 18/–. *A handy tool for the geologist.*

**Lithofacies Maps: An Atlas of the United States and Southern Canada.** L. L. SLOSS, E. C. DAPPLES, and W. C. KRUMBEIN. Pp. 108; figs. 5; maps, 153. Price, $5.50. John Wiley & Sons, New York, 1960. *Reconnaissance maps largely based on data taken from the stratigraphic literature, and surface and subsurface data on record in the Northwestern University Geology Department.*

**Cretaceous Stratigraphy of the Grand and Black Prairies, East-Central Texas.** Pp. 138; pls. 16; figs. 7. Price, $5.00. Baylor Geological Society Field Conference Guidebook, Waco, 1960. *While oil shows have been observed in several formations, the Paluxy sand (Comanchean series) is the only producing horizon and production is very low.*

**Third Annual Report of the International Tin Council, 1958–59.** Pp. 35. Price, $1.00. London. *Recovery from the production slump of late 1957 and 1958 due to export controls did not begin until the second quarter of 1959.*

**Science and Engineering in American Industry: Report on a 1956 Survey.** U. S. Dept. Labor, Bureau of Labor Statistics. Pp. 117; tbls. 13; charts 52. Price, 70 cents. National Science Foundation, Washington, 1959. *In the three year period from 1953 to 1956 the dollar volume of industrial research and development increased from 3.5 billion dollars to 6.2 billion dollars. Government contracts were chiefly responsible for this increase.*

**XXth International Geologic Congress, Mexico, 1956.**. *Reports on coal, tectonics of Sierra Madre, Vulcanology, Mesozoic of W. hemisphere, geology of petroleum, international committee on clays. Mexico, 1960.*

**The Australian Mineral Industry, Quarterly Review and Quarterly Statistics. Vol. 12, No. 3, March.** Pp. 22; tbls. 10. Price, 3/–. Bureau of Mineral Resources, Geology, and Geophysics, Canberra, 1960. *The increase in the production of zinc is expected to continue during 1960 and possibly 1961.*

**Belgian Congo—Comité Spécial du Katanga, Brussels, 1960. Topographic maps, degree sheets, scale 1/200,000 of Baudouinville, Zongwe, Kiambi, Kilwa, Kapulo, Moliro, Pweto.** *Non-contoured.*

**Mineral Economics and the Problem of Equitable Taxation.** OSCAR H. LENTZ. Pp. 111. Price, $1.00. Quarterly of the Colorado School of Mines, Vol. 55, No. 2, 1960. *While loopholes of tax avoidance may exist at present, i.e., where percentage-depletion rates are too high, the legislative rationale for percentage-depletion rates is sound.*

**Directory of Known Mining Enterprises, 1959.** FRANK A. CROWLEY. With a **List of Active Coal Mines, 1959** by THOMAS MORGAN and with a section on **The Mineral Industry of Montana in 1959** by F. B. FULKERSON and G. A. KINGSTON. Pp. 64; pl. 1; tbls. 4. Montana Bureau of Mines and Geology Bull. 14, Butte, 1960. *A decrease of 5 percent in the value of the 1959 mineral production from 1958 is attributed to a 4½ month strike at the Anaconda Company metal mines and metallurgical plants.*

**Ground Water in the Causey-Lingo Area, Roosevelt County, New Mexico.** JAMES B. COOPER. Pp. 51; pls. 2; figs. 13; tbls. 4. New Mexico State Engineer Office Technical Rept. 14, Santa Fe, 1960. *Principal ground-water source is unconsolidated sand and gravel of Cretaceous age, which fill erosion channels in the underlying Triassic red beds.*

**Geology and Ground-Water Resources of Rockland County.** NATHANIEL M. PERLMUTTER. Pp. 133; pls. 4; figs. 13; tbls. 18. New York Water Power and Control Commission, Bull. GW-42, Albany, 1959. *Principal aquifers are the Newark group and stratified drift. Water in the Newark group occurs mainly along bedding planes, joints, and fractures.*

**Oil In North Dakota Second Half 1959: Production Statistics and Engineering Data.** Pp. 89. Price $2.00. North Dakota Geological Survey, Grand Forks, 1960.

**Carbonatites of the Rufunsa Valley, Feira District.** D. K. BAILEY. Pp. 86; tbl. 1; appendices 6; plates 14; maps 4. Price L2 2s. *A detailed petrologic study of the carbonatites and Pre-and Karroo rocks in the title area. A section is devoted to the economic potentiality of the rare earth minerals associated with the carbonatite bodies.*

**Records of the Geological Survey of Tanganyika, Vol. 2, 1957.** Pp. 106; pls. 16; figs. 5; tbls. 17. Price, shs. 17/50. Dar Es Salaam, 1959. *Includes papers in economic and engineering geology.*

**Stratigraphy of the Blach Ranch-Crystal Falls Section (Upper Pennsylvanian), Northern Stephens County, Texas.** L. F. BROWN, JR. Pp. 45; pls. 3; figs. 6; tbl. 1. Bureau of Economic Geology, The University of Texas, Rept. of Investigations—No. 41, Austin, 1960. *Strata were deposited under cyclic, rapidly changing shallow marine to nonmarine conditions.*

**Bulletin of the Mineral Research and Exploration Institute of Turkey, Foreign Edition, Nos. 52, 53,** Ankara, 1959. *Articles on chrome, magmation, orogeny, basic igneous rocks, paleontology, uranium, tectonics, geophysics, sedimentation.*

**Geology and Ground-Water Resources of Pittsylvania and Halifax Counties.** HARRY E. LEGRAND. Pp. 86; pl. 1; figs. 6; tbls. 11. Virginia Division of Mineral Resources Bull. 75, Charlottesville, 1960. *Withdrawal of ground water is only a fraction of that available for recharge.*

**Geological Survey of Canada—Ottawa, 1960.**

**Paper 59-11. Horn River Map-Area, Northwest Territories.** R. J. W. DOUGLAS and A. W. NORRIS. Pp. 23; fig. 1; map 1; scale 1″/8 miles. Price, 50 cts. *Mainly a stratigraphic study of the Ordovician, Devonian and Cretaceous rocks of the Interior Plains.*

**Paper 59-12. Heavy-Metal (Zn, Pb, Cu) Content of Stream Sediments of Part of Westmorland County, New Brunswick.** ARTHUR Y. SMITH. Pp. 8; figs. 7. Price, 50 cts. *Methods of analyzing total extractable metals have resulted in detection of several anomalies in the Dorchester area.*

**Paper 59-15. Distribution of Some Reefs and Banks of the Upper Devonian Woodbend and Fairholme Groups in Alberta and Eastern British Columbia.** HELEN R. BELYEA. Pp. 7; map 1, scale 1″/20 miles. Price, 50 cts. *Seven pages of references accompany the reef distribution map.*

**Paper 59-16. On the Uranium Possibilities of the Southern Interior Plains of Canada.** J. A. CHAMBERLAIN. Pp. 8; fig. 1. Price, 25 cts. *A review of the sedimentary uranium deposits in the Interior Plains of the United States and Canada suggests little hope for uranium in the Canadian terrain.*

**Paper 60-5. Summary Account of Mesozoic and Tertiary Stratigraphy, Canadian Arctic Archipelago.** E. T. TOZER. Pp. 24; figs. 6; 1 correlation chart. Price, 50 cts. *Studies in the Sverdrup Basin have revealed the most complete Mesozoic-Tertiary section in the Arctic Archipelago.*

**Paper 60-10. Pleistocene Geology of Arctic Canada.** B. G. CRAIG and J. G. FYLES. Pp. 21; figs. 6; tbls. 1. Price, 50 cts. *The general Pleistocene geology is presented as a preliminary account with the valuable addition of 14 radiocarbon dates.*

**Memoir 302. Shubenacadie and Kennetcook Map-Areas, Colchester, Hants and Halifax Counties, Nova Scotia.** I. M. STEVENSON. Pp. 87; pls. 5; figs. 5; maps 2; scale 1″/1 mile. Price, $1.00. *A revised report on the stratigraphy, structure and economic deposits of central Nova Scotia.*

**Economic Geology Series No. 19. Mica Deposits of Canada.** J. W. HOADLEY. Pp. 136; tbls. 22; figs. 13. Price, $1.00. *A comprehensive study of mica deposits including uses, atomic structure, geology of mica and vermiculite deposits, domestic and foreign occurrences of mica, and the status of the Canadian mica industry.*

**Aeromagnetic Maps, Ontario, Nos. 910g–919g,** scale 1/63,360: **De Lesseps, Miniss, St. Joseph, Kawinogans, Dobie, Obabika, Kecheokagan, Mawley, Don-**

**nelly, N. Caribou. Geologic maps** (uncolored), preliminary series, scale 1/63,630. **Chilliwack and Quesnel Lake, British Columbia; Nichicun-Kaniapiskau, Quebec,** scale 1/506,880; **Vernon, British Columbia, Trout Lake, Ontario, British Columbia** (colored), scale 1/253,440. **Aeromagnetic Maps, Nova Scotia,** Nos. 784g–785g, 788g, 790g–792g, scale 1/63,360; **Chezzetcook, Musquodobit, Tatamagouche, Uniacke, Kennetcook, and Bass River.** Maps 925g–929g, **Ontario, Neverfreeze Lake, McCree Lake, Osnaburgh House, Ochig Lake, Tarp Lake, Mamiegowish Lake, Forester Lake, Opapimiskan Lake, Wachusk Lake, and Menako Lakes.**

**Univ. California Publications in Geological Sciences—Berkeley, 1960.**

**Vol. 34, No. 5. Origin of Rock Creek and Owens River Gorges, Mono County, California.** WILLIAM C. PUTNAM. Pp. 221–280; pl. 31–40; figs. 3; maps 3. Price, $2.00. *Both gorges were probably eroded due to increased discharge of the occupying rivers as they captured major water sources through headward growth.*

**Vol. 36, Nos. 3 and 4. Ohlson Ranch Formation, Pliocene, Northwestern Sonoma County, California.** CHARLES G. HIGGINS. Pp. 199–232; pls. 3; figs. 6; map 1. **Paleontology and Correlation of the Ohlson Ranch Formation.** JOSEPH H. PECK, JR. Pp. 233–242; pl. 1. Price, $1.50. *This formation is essentially a shallow-water terrace deposit. The fauna suggest that sea-surface temperatures were somewhat warmer than at the present.*

**Fiji Geological Survey—Suva, 1959–1960.**

**Bull. 5. Geology of Savusavu Bay West, Vanua Levu.** R. W. BARTHOLOMEW. Pp. 28; pls. 12. Map, scale 1/50,000. Price, 12s. 6d. *A small open-cut gold mine was worked from 1932 to 1944. It yielded 63,770 oz. of gold and 4,830 oz. of silver.*

**Annual Report for the Year 1959.** Pp. 21; maps 3. Price, 2s. *Interest is developing in bauxite exploration.*

**Geological Survey of India—Delhi, 1958–1959.**

**Bull. 15. The Manganese-Ore Deposits of Panch Mahals and Baroda Districts, Bombay State.** B. C. ROY. Pp. 43; pls. 10. Price, Rs. 3.25 or 5sh. 3d. *The principal types of ore deposits are 1) regional, progressive replacements, 2) veins, 3) manganiferous laterite gravels or soils, and 4) concentrations along fractures.*

**Bull. 16. High Grade Limestone Deposits, Dehra Dun—Mussoorie Area, U. P.** D. R. S. MEHTA, R. N. MURTHY, and A. S. MARASIMHAN. Pp. 51; tbls. 27; pls. 6. *The limestone deposits occur in the Upper Krol rocks. The limestone with CaO between 50–55% is considered chemical grade and there are quarriable reserves of 143 million tons.*

**Bull. 17. The Manganese-Ore Deposits Near Joida, North Kanara District.** B. C. ROY and Y. S. SAHASRABUDHE. Pp. 24; pls. 7. Price, Rs. 2.50 or 4 sh. *The manganese ore is associated with the weathering of the Dharwars rocks and the formation of lateritic soils.*

**Ohio Department of Natural Resources—Columbus, 1959.**

**Water Plan Inventory Rept. 6. Water Use in Ohio.** ANTHONY R. RUDNICK. Pp. 60; pls. 6; tbls. 11. Price, 50 cts. *Ohio has enough water for its future needs*

*if managed properly. Shortages may occur through failure to solve administrative and other similar problems.*

**Water Plan Inventory Rept. 7. Irrigation and Rural Water Use in Ohio.** ARTHUR F. WOLDORF. Pp. 57; pls. 6; figs. 10; tbls. 8. Price, 50 cts. *At present, irrigation of golf courses requires more water than is used for irrigation by all the farms in the state.*

**U. S. Geological Survey—Washington, D. C., 1959–1960.**

**Bull. 1028-0. Geologic Reconnaissance of Semisopochnoi Island, Western Aleutian Islands, Alaska.** ROBERT R. COATS. Pp. 477–519; pl. 10; figs. 4; tbl. 1. Price, $1.25. *The island consists entirely of Pleistocene and Recent basaltic volcanics and derived sediments.*

**Bull. 1028-P. Geology and Submarine Physiography of Amchitka Island, Alaska.** H. A. POWERS, R. R. COATS, and W. H. NELSON. Pp. 521–554; pl. 1, figs. 2; tbl. 1. *The bedrock of Amchitka Island ranges in age from pre-Oligocene to Pleistocene.*

**Bull. 1028-Q. Geology of Rat Island, Aleutian Islands, Alaska.** R. Q. LEWIS, W. H. NELSON, and H. A. POWERS. Pp. 555–562; pl. 1; fig. 1. Price, 35 cts. *The geology of Rat Island, in the western Aleutians, consists of an older series of andesite flows and breccias overlain by basaltic flows and tuffs.*

**Bull. 1071-D. Geology of the Huerfano Park Area, Huerfano and Custer Counties, Colorado.** ROSS B. JOHNSON. Pp. 87–119; pls. 6; fig. 1. Price, $1.25. *A study of the compressional effects on the sedimentary rocks of thrusting toward an area of vertical uplifting.*

**Bull. 1071-E. Geology of the Lower Marias River Area, Chouteau, Hill, and Liberty Counties, Montana.** J. F. SMITH, JR., I. J. WITKIND, and D. E. TRIMBLE. Pp. 121–155; pls. 3; figs. 4. *The bedrock is of Late Cretaceous age ranging from the Colorado Shale to the Judith River formations. Two tills are recognized in the Pleistocene deposits.*

**Bull. 1072-K. Geology and Oil and Gas Possibilities of Upper Mississippian Rocks of Southwestern Virginia, Southern West Virginia, and Eastern Kentucky.** R. H. WILPOLT and D. W. MARDEN. Pp. 587–656; pls. 3; figs. 7; tbl. 1. *The results of stratigraphic fieldwork during 1948 and of studies of subsurface stratigraphy during 1949 are presented.*

**Bull. 1072-L. Distribution of Silica Resources in Eastern United States.** T. D. MURPHY. Pp. 657–665; pls. 9. *Text includes definitions and uses of silica raw materials and states industrial specifications. Maps show location of silica resources and operations.*

**Bull. 1072-M. Geology and Fuel Resources of the Mesa Verde Area, Montezuma and La Plata Counties, Colorado.** ALEXANDER A. WANEK. Pp. 667–721; pls. 13; fig. 1; tbls. 7. *The rocks exposed are of late Cretaceous age ranging from the Dakota sandstone to Cliff House sandstone. Oil and gas possibilities are discussed.*

**Bull. 1076. The Square Buttes Coal Field, Oliver and Mercer Counties, North Dakota.** W. D. JOHNSON, JR., and R. P. KUNKEL. Pp. 92; pls. 7; figs. 4; tbls. 6. *Coal reserves in the Fort Union formation in the Square Buttes field are estimated to be 3 billion tons in beds 2½ feet or more thick.*

**Bull. 1087-D. Geology and Uranium Deposits of Monument Valley, San Juan County, Utah.** R. Q. LEWIS, SR., and D. E. TRIMBLE. Pp. 105–131;

pls. 4; figs. 6; tbls. 3. Price, $1.00. *All the uranium vanadium deposits in the Monument Valley area are restricted to the lower channel sediments of the Shinarump member of the Chinle formation.*

**Bull. 1095. Bibliography of North American Geology, 1957.** RUTH R. KING, VIRGINIA M. JUSSEN, ELISABETH S. LOUD, and GEORGIANNA D. CONANT. Pp. 531. Price, $1.75.

**Bull. 1105. Selected Annotated Bibliography of Gypsum and Anhydrite in the United States and Puerto Rico.** C. F. WITHINGTON and MARION C. JASTER. Pp. 126. *More than 400 annotated references, to January, 1959, on the geology, geographic occurrences, origin, technology, and uses of gypsum and anhydrite.*

**Bull. 1106-D. Geophysical Abstracts 179, October–December, 1959.** DOROTHY B. VITALIANO, S. T. VESSELOWSKY, and others. Pp. 407–531. Price, 40 cts.

**Bull. 1109. Geologic Appraisal of Dimension-Stone Deposits.** L. W. CURRIER. Pp. 78; pls. 7; figs. 2; tbls. 4. *A background and field guide for the geologic study of commercial stones.*

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**Prof. Paper 354-C. Giant Waves in Lituya Bay, Alaska.** DON J. MILLER. Pp. 51–86; pls. 9; figs. 7; tbls. 1. *The relatively frequent occurrence of giant waves in Lituya Bay is attributed to the combined effect of recently glaciated steep slopes, highly fractured rocks and deep water in an active fault zone, heavy rainfall and frequent freezing and thawing.*

**Water-Supply Paper 1457. Ground-Water Conditions in the Avenal-McKittrick Area, Kings and Kern Counties, California.** P. R. WOOD and G. H. DAVIS. Pp. 141; pls. 5; figs. 10; tbls. 10. *In most areas the high sodium (mostly sulfate) content of the groundwaters make them of doubtful quality for irrigation.*

**Water-Supply Paper 1458. Geology and Ground-Water Resources of the Rawlins Area, Carbon County, Wyoming.** D. W. BERRY. Pp. 74; pl. 1; figs. 5; tbl. 1. *In the vicinity of Rawlins copious water supplies are available from the Cloverly formation, Tensleep sandstone, Madison limestone, and Cambrian rocks.*

**Water-Supply Paper 1484. Geology and Ground-Water Features of Shasta Valley, Siskiyou County, California.** SEYMOUR MACK. Pp. 115; pls. 2; figs. 12; tbls. 23. *The Plutos Cave basalt constitutes the principal aquifer yielding an average of 1300 gallons per minute.*

*Economic Geology*
Vol. 55, 1960, p. 1081–1082

# SCIENTIFIC NOTES AND NEWS

U. S. Geological Survey scientists at the Hawaiian Volcano Observatory have been observing a slowly cooling pond of molten lava in Kilauea Iki. A crust thick enough and cool enough to walk on has formed over the 2,500-foot diameter 365-foot deep lava pond following the November–December activity. By the end of April a hole 7½-feet deep has been put down into the crust with a small electric drill and a carbide-tipped bit. The crust had then solidified to a depth of about 10 feet and could be walked on. The temperature at a depth of two feet was about 500° Fahrenheit; at four feet it was about 940°F; at six feet, 1250° and at 7½ feet, 1400°, indicating a variation of about 210°F per foot. At 12¾ feet the temperature is 1685°F, and a red glow is visible toward the bottom. Below this the carbide-tipped masonry drill disintegrates at this high temperature. It is quite apparent that molten lava must be only a few feet further down.

The Honolulu Magnetic and Seismological Observatory recently constructed at Ewa Beach, Island of Oahu, Hawaii, was dedicated Thursday, June 23, 1960. The new observatory will serve as the Bureau's principal geomagnetic station in the Pacific, and will be a vital link in the Survey's vast program of locating earthquakes throughout the world. It will continue to function as the nerve center of the extremely important Seismic Sea Wave Warning System in the Pacific.

G. Dessau who had, by the end of 1957, completed his main UNESCO assignment with Technion, Israel Institute of Technology in Haifa has since then been at the University of Pisa, Italy, in charge of a course on Mineral Deposits. At the beginning of 1960 he left Pisa temporarily to spend a year as a Research Fellow at the Division of Geological Sciences of Harvard University under a Fulbright grant and a grant from the Italian Council of Scientific Research. He is working on sulfur ores from Sicily.

The Earthquake Engineering Research Institute and the California Institute of Technology under an emergency grant from the National Science Foundation have sent a team of scientists and engineers to Chile to collect data on the disastrous earthquakes there. Since this probably was the greatest series of earthquakes in history, valuable scientific and engineering information should be forthcoming from the study.

Walter Stoll, professor of economic geology at the University of Buenos Aires, has been appointed consultant in geology and mining to the Pan American Union, Organization of American States.

Gold medals of the Institution of Mining and Metallurgy for 1960 have been awarded to Edward Duffield McDermott and to Julius Kruttschnitt.

Quentin D. Singewald is on leave from the USGS and has started a two year tour of duty with International Cooperation Administration to serve as geological adviser to the Institute of Applied Geology of the University of Istanbul, Turkey.

Spencer S. Shannon has resigned as director of the government's Office of Minerals Mobilization.

Vincent D. Perry has been elected to the board of directors of Greene Cananea Copper Company, the Sonora, Mexico subsidiary of the Anaconda Company. He has been associated with Anaconda's mining and geological activities since 1922

and has been vice president and chief geologist of the Anaconda Company since 1957.

JOHN M. MOORE, JR. has been selected for the Queen Elizabeth II Fellowship for original research in earth sciences.

## SOCIETY OF ECONOMIC GEOLOGISTS

The 1960 Nominating Committee—D. F. Kidd, Chairman, James Boyd, and Carl Tolman—has nominated, and the Council has approved the nomination of the following slate to serve as officers of the Society of Economic Geologists for the terms and offices indicated:

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| North America | J. Ruben Velasco |
| South America | Robert D. Butler |
| Councilors, 1961–63 | Ernest L. Ohle |
| | Frederick S. Turneaure |
| | Alfred W. Jolliffe |

In accordance with Article III of the By-Laws (as amended 1959), the ballot for election of officers will be sent to the membership in October.

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*For description of Professor Sampson's method, see Economic Geology, Vol. 51, No. 5, August, 1956.* *Write for Bulletin*

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